CHEMISTRY OF CONJUGATED MONOMERS IN ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION

By

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This dissertation is dedicated to my parents
for their love and support.

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CHEMISTRY OF CONJUGATED MONOMERS IN ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION

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April, 1994

Chairman: Dr. Kenneth B. Wagener
Major Department: Chemistry

A study of the chemistry of conjugated monomers, such as 2,4-hexadiene and dipropenylbenzene, in acyclic diene metathesis (ADMET) polymerization is presented. Conjugated polymers and their copolymers have been synthesized through ADMET polymerization of corresponding monomers using well-defined alkylidene complexes of the type $M(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCH_3(CF_3)_2]_2$ (M=W or Mo; R=CMe_3 or CMe_2Ph) as catalysts.

Methyl-terminated polyacetylene oligomers were successfully synthesized through the ADMET polymerization of the internal conjugated dienes, 2,4-hexadiene and 2,4,6-octatriene. Solution polymerization of 2,4-hexadiene produced a longer polyacetylene chain than did bulk polymerization of the same monomer. The terminal diene and triene, 1,3-butadiene and 1,3,5-hexatriene, were

not productive in ADMET polymerization, since the molybdenum catalyst was decomposed by the monomers. Block poly(acetylene-co-octenamers) were obtained through copolymerization of 2,4-hexadiene and 2,10-dodecadiene.

Telechelic polyacetylenes were synthesized through ADMET polymerization of 2,4-hexadiene with internal monoolefins, such as 7-tetradecene, propenyl benzene, 1,4-bis(trimethylsilyl)-2-butene, and 4-octene-1,8-diyl acetate, but not with terminal monoolefins. The ADMET polymerization of functional group-terminated 1,3-butadienes was not successful, either because of steric hindrance prohibiting the ADMET reaction or because of a non-productive reaction stopped ADMET polymerization.

Poly(1,2-phenylene vinylene) and poly(1,3-phenylene vinylene) oligomers were synthesized through ADMET polymerization of 1,2-dipropenylbenzene and 1,3-dipropenylbenzene, respectively. The copolymerization of 1,2-dipropenylbenzene and 1,3-dipropenylbenzene with 1,9-decadiene produced copolymers having random statistical structural distributions based on the initial monomer feed ratios. Block poly(1,2-phenylenevinylene-co-octenamer) was obtained through the addition of 1,9-decadiene to poly(1,2-phenylene vinylene); the addition of 1,2-dipropenylbenzene to polyoctenamer, however, produced a random copolymer.

CHAPTER 1

INTRODUCTION

Polymer science and technology have had a profound influence on the quality of life in the 20th century. Indeed polymeric materials, from plastics and synthetic fibers to synthetic rubbers, can be seen everywhere in daily life. They are also widely used in industry as engineering materials to replace traditional, naturally occurring materials, such as metals and cellulosic compounds, because of their relative ease of manufacture and fabrication, wide range of physical and chemical properties, and low raw material cost.

The pioneering work of Staudinger, Mark, Carothers, and others in the 1920s and 1930s[1-8] has laid the foundation for the "plastic age" by establishing molecular principles governing the formation and properties of polymers. These early workers paved the way for the rich variety of synthetic polymers that have characterized the last 60 years.

This dissertation deals with the new polymerization chemistry, known as acyclic diene metathesis (ADMET) polymerization. The research represents an effort to extend ADMET polymerization to conjugated monomers in which two olefins are connected together or are connected by a phenylene group. The polymerizability and reactivity of the conjugated monomers are

investigated, and the basic physical and chemical properties of synthesized conjugated polymers, polyacetylene, poly(phenylene vinylene), and their derivatives are examined.

A literature review is presented first in order to obtain a better understanding of these conjugated polymers and of ADMET polymerization, as it is related to metathesis chemistry and metal catalysts.

The Syntheses, Properties and Applications of Polyacetylene (PA) and Poly(phenylene vinylene) (PPV)

Conjugated polymers (Figure 1.1) are currently attracting considerable interest because of their conducting and nonlinear optical properties. They have a wide variety of applications including high power rechargeable batteries, electronic devices, and nonlinear optical devices, and even as potential replacements for metal wires.

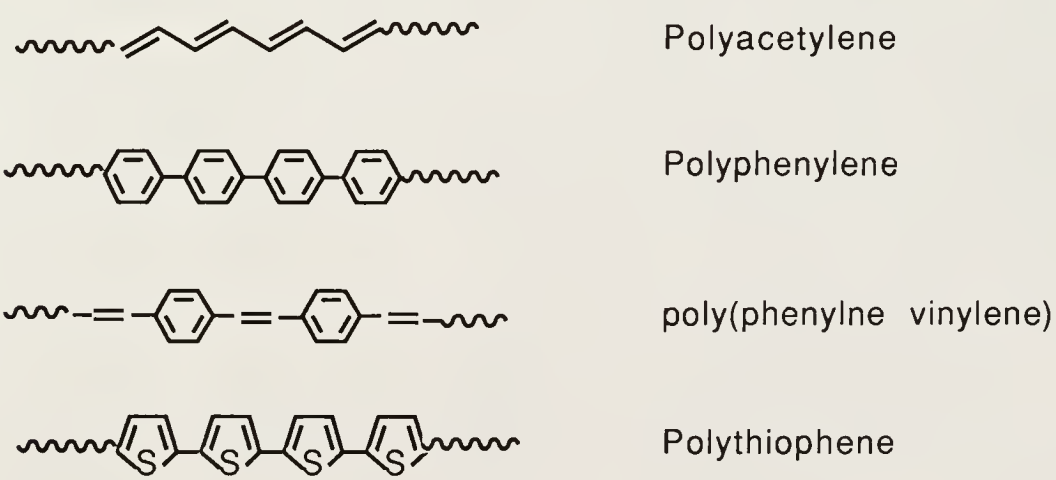


Figure 1.1. Four examples of conjugated polymers.

From a materials science point of view, conducting polymers represent an attempt to combine the electrical behavior of metals with the mechanical properties of plastics. The versatility, environmental stability, ease of fabrication, and light weight of conducting polymers make them fascinating materials for electronic devices.

Since Ito, Shirakawa and Ikada[9] first synthesized free-standing, silvery polyacetylene film in 1974 and found that it had high conductivity, extensive theoretical and experimental research has been devoted to this polymer, which has kept polyacetylene research as one of the most active areas of study. The conductivity of polyacetylene can be manipulated over an enormous range of values, from insulator (10^{-12} mho/cm) to good conductor (10^{3} mho/cm), by doping.

Conjugated polymers inherently possess a very high nonlinear optical (NLO) response.[10-18] In trans polyacetylene, photoexcitation across the gap produces electron hole pairs that are found to decay very rapidly (in 10^{-3} sec) into pairs of separated, positively and negatively charged, solitons.[19-23] It is important to note that this process results in an efficient charge separation mechanism, a feature essential for providing large optical nonlinearities.[24-26] The large values of third order susceptibility ($c^{(3)}(w)$) in short polyacetylene oligomers (also called polyenes) has historically been important because they are the simplest conjugate system.[27] Drury[28] reported in samples of oriented fully dense polyacetylene a highest third order nonlinear optical susceptibility, $c^{(3)}$, in excess of 10^{-8} esu.

Polyacetylene can also be used as a gas separation membrane, such as the membrane of a disubstituted polyacetylene, poly[1-(trimethylsilyl)-1-propyne] [P(TMSP)]. The P(TMSP) membrane prepared by solvent casting shows extremely high permeability for oxygen and nitrogen gases.[29-31] For example, the permeability coefficient for oxygen through the glassy P(TMSP) membrane at room temperature is about 10 times as high as that through polydimethylsiloxane membrane, which had been known to show the highest value among nonporous polymer membranes.[32]

Polyene chains (short length of polyacetylene) are also important components of natural products,[33-36] such as a wide variety of natural carotenoids found in fruits, vegetables, and poultry.

The first linear conjugated polyacetylene was synthesized from acetylene by Natta, Mazzanti, and Corradini[37] in 1958 using a $Ti(OBu)_4/AlEt_3$ catalyst at a low concentration of a few millimolars of monomer. They obtained an insoluble, infusible, gray powder. Later, a number of polyacetylenes were synthesized using transition metal catalysts with varying degrees of efficiency.[38-40] With the same $Ti(OBu)_4$-$AlEt_3$ catalyst but varying concentration, solvent, and reaction temperatures, Hatano *et al.*[41] were able to prepare polyacetylene with varying degrees of crystallinity, and less than 1% of the reaction led to benzene.[42] It appears that this catalyst produces higher yields of linear polyacetylene than other systems investigated.

Block and graft acetylene copolymers have been produced through a number of synthetic techniques. The preparation of

acetylene block copolymers via anionic, Ziegler-Natta, and metathesis polymerization methods has been reported.[43-47] An example of the formation of poly(acetylene-co-styrene) through Ziegler-Natta polymerization is illustrated in Figure 1.2, where a double-labeling experiment, utilizing ^{14}C and tritium, was employed to show that copolymer, not polyacetylene homopolymer, was forming.[44] Graft copolymers were synthesized where either a growing polyacetylene chain in solution was grafted onto a solubilized carrier polymer, or the chain was polymerized off the carrier polymer as a side chain.

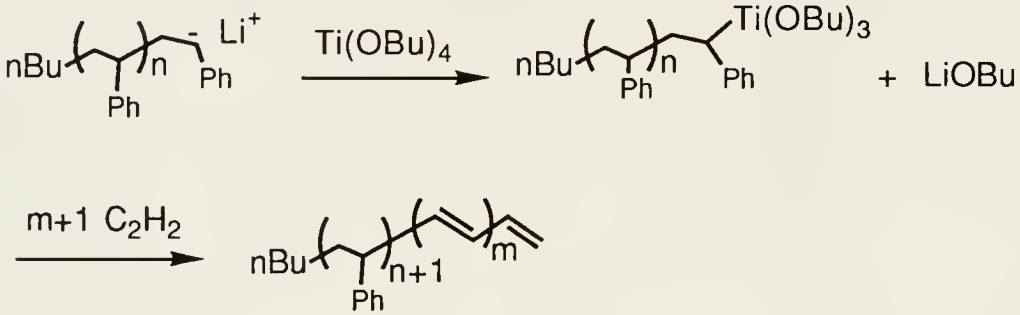


Figure 1.2. Copolymerization of acetylene and styrene using $Ti(OBu)_4$ as catalyst.

Syntheses of polyacetylenes through ring opening metathesis polymerization and acetylene metathesis polymerization will be discussed later in this chapter.

Polyacetylene is usually a gray or black semicrystalline powder which is insoluble in any solvent and decomposes before melting.[48] Polyacetylene is a very reactive macromolecule being extremely sensitive to heat, oxygen, and other unknown aging processes. Natural abundance ^{13}C nuclear magnetic resonance (NMR)

spectra have been obtained with cross polarization and magic angle spinning by several groups,[49-51] who have determined that the trans-polyacetylene chemical shift is 136 to 139 ppm downfield from tetramethylsilane (TMS), while the shift for cis-polyacetylene is 126 to 129 ppm.

Poly(phenylene vinylene) (PPV) represents a combination of chemical structures between polyphenylene (PPP) and polyacetylene (PA) and has the favorable electronic properties of these two prototype polymers (Figure 1.3). For a long time poly(phenylene vinylene) has also served as a model for the analogous polyphenylenes and polyacetylenes.[52-55] Poly(phenylene vinylene) is a photoconductor with a band gap of 2.4 eV,[55] and its high conductivity can be reached by appropriate chemical or electrochemical treatment.

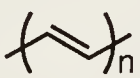
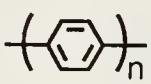
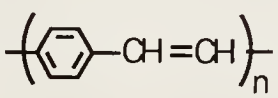
Polymer	Structure	Eg (ev)	IP (ev)
Polyacetylene		1.5	6.7
Poly(1,4-phenylene)		3.2	7.5
Poly(phenylene vinylene)		2.4	7.0

Figure 1.3. The structures of polyacetylene, poly(1,4-phenylene), and poly(phenylene vinylene), and their band gap (Eg) and ionization potential(IP).[55]

Poly(phenylene vinylene) has been synthesized using either a Wittig condensation or a dehydrohalogenation reaction,[56] but only

oligomers were formed in these reactions. Wessling and Zimmerman[57] and Kanbe and Okawara[58] in 1968, and later, Capistran *et al.*,[59] Gagnon *et al.*,[60] Murase *et al.*,[61,62] reported using a soluble precursor polymer for the preparation of PPV. The method (Figure 1.4) involves preparation of a bis-sulfonium salt for the parent PPV followed by an elimination-polymerization reaction to produce an aqueous solution of precursor polymer. This polymer can be processed into films, foams, and fibers.[57-61] Heating a cast film of precursor polymer at 200 °C for more than 2 h results in a yellow free-standing film of PPV.

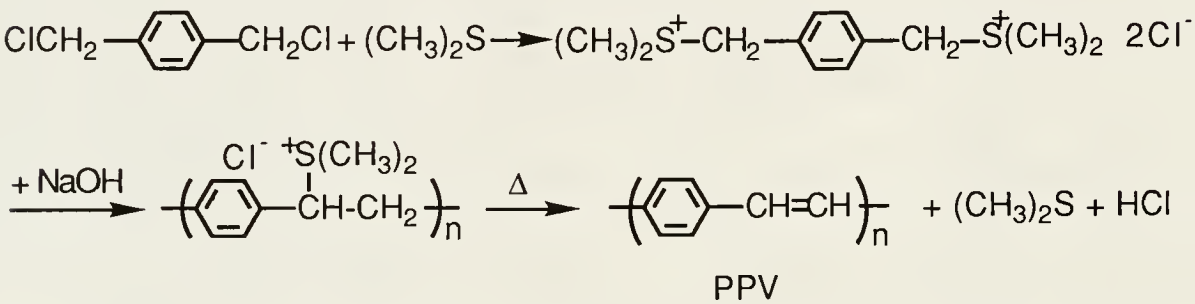


Figure 1.4. A scheme for the preparation of PPV by the precursor method.

Unsubstituted PPV appears to be yellow, whereas cyano and methoxy substitution cause a color shift to orange and deep red. On the other hand, phenyl substitution changes absorption to light yellow. When PPV was examined by differential scanning calorimetry (DSC), no glass or melt transition was observed between -196 °C and 500 °C. Decomposition begins at about 550 °C in a nitrogen atmosphere.[63] Stenger-Smith *et al.*,[64] reported that the PPV from poly[p-phenylenedimethylene-α-tetrahydrothio-phenium

chloride] shows a slightly longer UV/vis wavelength absorption maximum, because the polymer has fewer sp^3 hybridized carbon atoms, and therefore longer conjugation lengths in the polymer.

Historical Development of Olefin Metathesis Chemistry

The olefin metathesis reaction is considered as a very successful organic reaction with many applications in both the low molecular weight range and the polymer field. No one would have predicted in the 1950s or early 1960s that a reaction in which the double bond is apparently cleaved and the pieces reassembled was even remotely possible. Yet not only is it possible, but also in some cases it can proceed to equilibrium within seconds.

The word "metathesis" is originally from the Greek meta meaning "change" and tithemi meaning "place." Metathesis in chemistry refers to the interchange of two parts of two substances to form two new substances, such as the metathesis reaction between salts, acids, and bases in inorganic chemistry. The term "olefin metathesis" is commonly used to express the interchange of carbon atoms between a pair of double bonds[65] resulting in the formation of two new olefins (Figure 1.5).

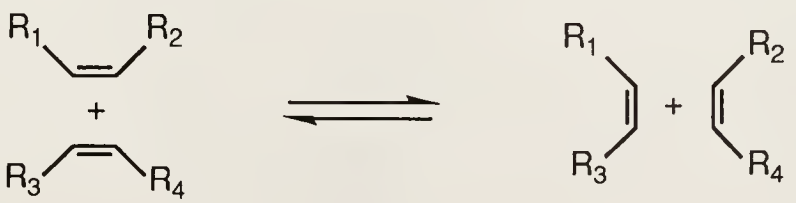
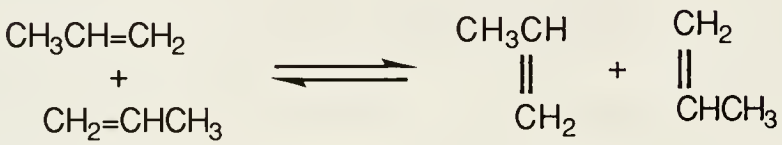


Figure 1.5. General olefin metathesis reaction.

Olefin metathesis reactions are classified into three basic categories: (1) the exchange reaction, of which two types are known, productive and degenerate (Figure 1.6); (2) degradation reactions (Figure 1.7);[65,66] and (3) polymerization reactions, of both ring opening and condensation types (Figure 1.8).

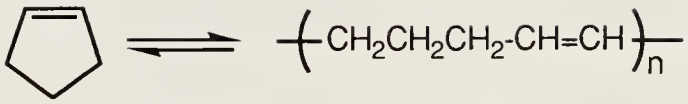
(a) Productive metathesis.



(b) Degenerate metathesis.

Figure 1.6. Olefin exchange metathesis reaction.

Figure 1.7. Degradation metathesis reaction.



(a) Ring opening metathesis polymerization (ROMP).

(b) Acyclic diene metathesis (ADMET) polymerization.

Figure 1.8. Metathesis polymerizations.

The expression "olefin metathesis" was coined by Calderon in 1967,[66] and until that time the chemistry of exchange reactions and ring opening metathesis polymerization had developed independently. The first metathesis work was the ring opening metathesis polymerization of cyclopentene and norbornene on MoO_3/Al_2O_3 and activated with $LiAlH_4$ in 1957.[67] This was followed in 1960 by an open publication from the same laboratories describing the ring opening metathesis polymerization (ROMP) of norbornene on $TiCl_4$/ $LiAlR_4$.[68] Soon afterwards it was discovered by Natta's group that cyclobutene[69] and cyclopentene[70] would undergo ROMP in the presence of $TiCl_4/Et_3Al$, $MoCl_3/Et_3Al$, or WCl_6/Et_3Al, even at a low temperature(-50 °C), and that the fraction of *cis* double bonds was dependent on the conditions. $RuCl_3$ was also found to be effective in conducting ROMP of cyclobutene and its derivatives in water or alcohol.[71] In the meantime, following the first patent[72] in 1960 which disclosed the disproportionation of propene on $MoO_3/Al_2O_3/Bu_3Al$, Banks and Bailey[73] in 1964 gave the first definitive account of the disproportionation of acyclic olefins on

$Mo(CO)_6/AL_2O_3$, operating at 160 °C. The metathesis of propene (Figure 1.9) was subsequently developed as an industrial process, and beginning in 1966 this process was operated for 6 years by Shawinigan Chemical Co. in Montreal.

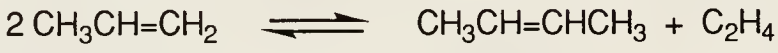


Figure 1.9. Metathesis reaction of propene.

In 1967, Calderon *et al.*[66,74] made the important discovery that the catalyst system $WCl_6/EtAlCl_2/EtOH$ (1/4/1) would cause not only the very rapid ROMP of cyclopentene but also the disproportionation of 2-pentene at room temperature. This discovery provided the bridge that led to the realization that these were examples of one and the same chemical reaction.[74] Furthermore, the reaction between 2-butene and 2-butene-d_8 led only to 2-butene-d_4 (Figure 1.10), demonstrating that the double bonds themselves were completely broken in the chemical reaction.[75,76]

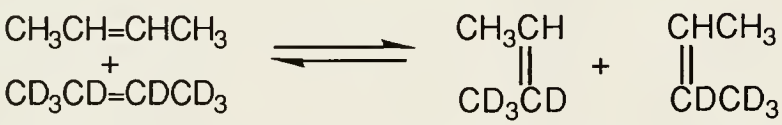


Figure 1.10. Metathesis disproportionation reaction.

The cross metathesis between a cyclic and acyclic olefin was first reported in a patent[77] in 1966 using a moblydenum-based catalyst (Figure 1.11).

Figure 1.11. Cross metathesis reaction.

Olefin metathesis reactions do not occur spontaneously. They all require a catalyst system.[65,78] The early metathesis catalyst systems closely resemble a Ziegler-Natta polymerization catalyst mixture, which are later referred to as "classical catalysts." Those catalysts are based upon 11 transition metals: Ti, Zr, and Hf (group IVA); Nb and Ta (group VA); Mo and W (group VIA); Re (group VIIA); Ru, Os, and Ir (group VIIIA). The most effective catalysts have either Mo, W, or Re as the active metal center.

The "classical" olefin metathesis catalysts consist of a heterogeneous or homogeneous transition metal compound, frequently in conjunction with a Lewis acid as co-catalyst and sometimes a third promoter.[79,80] Many more complex multi-component formulations have also been investigated with the goal of controlling selectivity which has been reviewed in detail in Ivin's book.[65] Examples of homogeneous catalyst formulations are $[Mo(NO_2(L)_2Cl_2]$-$[R_3Al_2Cl_3]$[81-84] (L=PPh_3; R=Me, Et), WCl_6-EtOH,[77,85] $WOCl_4$-$SnMe_4$,[86] $MeReO_3$-$AlCl_3$,[87] and $[Re(CO)_5Cl]$-$EtAlCl_2$.[88] Many of these and closely related species have also been supported on polymer resins.[89-91]

The Metal Carbene Mechanism

Once it was clear that the double bonds themselves were being broken in the olefin metathesis reaction, different mechanisms were proposed by chemists to explain the metathesis reaction processes. Natta *et al.*[92] originally proposed a mechanism involving the cleavage of the alpha carbon-carbon σ bonds, which was not accepted by later chemists. In 1967, Bradshaw *et al.*[93] suggested a "quasicyclobutane" intermediate in an attempt to explain the disproportionation metathesis reaction of propene (Figure 1.12), a report in which they claimed that there was not enough information to propose an actual mechanism.

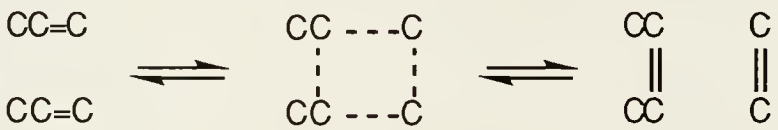


Figure 1.12. Bradshaw's quasicyclobutane intermediate proposed for the metathesis disproportionation of propene.

Later, Calderon and coworkers,[74-75] offered additional support and detailed investigation for this mechanism and proposed that the transition metal provided orbitals that overlapped those associated with the two carbon-carbon double bonds in such a way as to facilitate metathesis via a weakly held cyclobutane-type complex. This mechanism, which became known as "pairwise mechanism" (Figure 1.13), explained the metathesis reaction so well that it gained general acceptance at that time. This mechanism, however, has since been proven inaccurate.

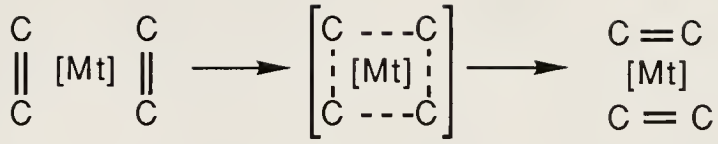


Figure 1.13 Calderon pairwise mechanism for olefin metathesis.

Since 1975, evidence in favor of the metal carbene mechanism has become so compelling that the pairwise mechanism has been finally abandoned. The non-pairwise or metal carbene mechanism suggests that the reaction occurs through a reversible [2+2] cycloaddition of a carbon-carbon double bond to a metal carbene to form a metallacyclobutane intermediate, which can then cleave to produce a new olefin (Figure 1.14). A metal carbene is regenerated at every stage.

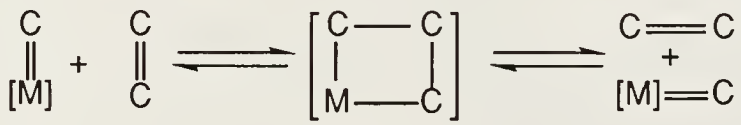
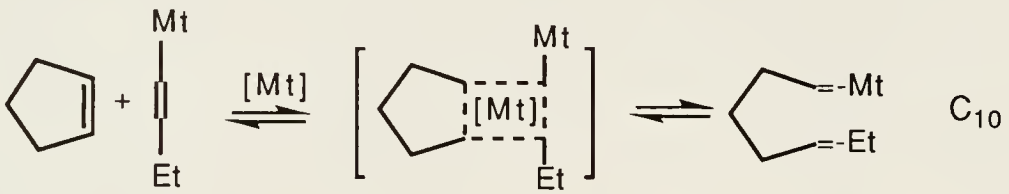


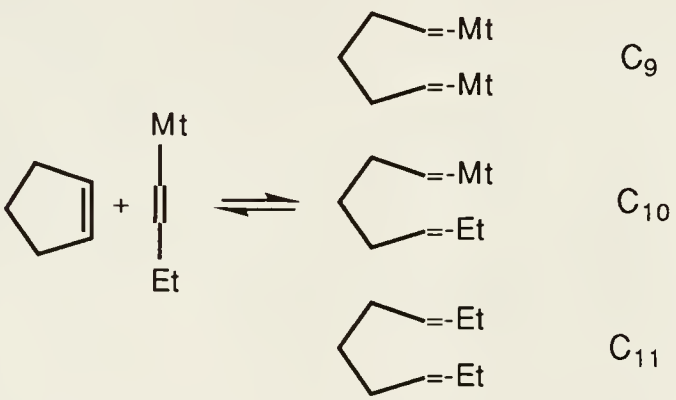
Figure 1.14 The metal carbene mechanism of olefin metathesis reaction.

The carbene mechanism was first proposed in 1970 by Herisson and Chauvin[94] on the basis of cross-metathesis experiments using cyclopentene and an unsymmetric olefin, 2-pentene (Figure 1.15). The statistical product mixture obtained in this reaction is difficult to explain by the pairwise reaction mechanism, since it would lead one to expect that the cross reaction between cyclopentene and 2-pentene would initially produce only one product, C_{10}, as shown in Figure 1.15 (a). In fact, using

$WOCl_4/Bu_4Sn$ and $WOCl_4/Et_2AlCl$ in chlorobenzene as catalysts, Herisson and Chauvin found three products (C_9, C_{10}, and C_{11} in Figure 1.15 (b)) in the statistical ratio 1:2:1, even in the initial products, and it was this observation that led them to propose the metal carbene chain mechanism. Similar results were obtained with cyclooctene, 1,5-cyclooctadiene, and 1,5,9-cyclododecatriene in place of cyclopentene.



(a) Cross-metathesis reaction through pairwise mechanism.



(b) Cross-metathesis reaction through metal carbene mechanism.

Figure 1.15. Cross-metathesis reaction of cyclopenetene and 2-pentene through different mechanism.

The formation of the three series of products could be explained in terms of the following sequence of reactions (Figure 1.16), where 2-pentene represented as Q^1Q^2 [Q^1=ethylidene (MeCH=);

Q^2=propylidene (EtCH=)], cyclopentene represented as M, metal catalyst represented as [Mt], and $Q^1M_nQ^1$, $Q^1M_nQ^2$ (equal to $Q^2M_nQ^1$), and $Q^2M_nQ^2$ are the three series of products. In a more detailed study of this type reaction, Katz and McGinnis[95] found that in the case of cyclooctene/2-hexene, the initial ratio of the three products, as determined by extrapolation to zero time, was 1:3.2:1 (C_{12}:C_{14}:C_{16}). A more clear-cut experiment is to react cyclooctene with a mixture of 2-butene and 4-octene, a "double cross-metathesis" reaction. Using $MoCl_2(NO)_2(PPh_3)_2/Me_3Al_3Cl_3$ in chlorobenzene as catalyst, Katz and McGinnis found that the initial product ratio (C_{14}/C_{12})(C_{14}/C_{16}) was 4.05±0.05 for cis reactants and 4.11±0.09 for trans reactants, compared with predicted values of 4.0 for the metal carbene mechanism, zero for the simple pairwise mechanism, and about 2.7 for the pairwise, sticky-olefin mechanism. This experiment shows clearly that all types of pairwise mechanisms must be rejected.

$$[Mt]{=}Q^1 + n\ M \longrightarrow [Mt]{=}M_nQ^1 \qquad (1)$$

$$[Mt]{=}M_nQ^1 + Q^1Q^2 \rightarrow \begin{cases} [Mt]{=}Q^2 + Q^1M_nQ^1 & (2) \\ [Mt]{=}Q^1 + Q^2M_nQ^1 & (3) \end{cases}$$

$$[Mt]{=}Q^2 + n\ M \longrightarrow [Mt]{=}M_nQ^2 \qquad (4)$$

$$[Mt]{=}M_nQ^2 + Q^1Q^2 \rightarrow \begin{cases} [Mt]{=}Q^1 + Q^2M_nQ^2 & (5) \\ [Mt]{=}Q^2 + Q^1M_nQ^2 & (6) \end{cases}$$

Figure 1.16. A cross-metathesis reaction sequence.[65]

Ring opening metathesis polymerization offers more evidence for the metal carbene mechanism. The products of the ROMP reaction generally consist of a high molecular weight fraction, often having a molecular weight in excess of 10^5, and a low molecular weight fraction consisting of a series of cyclic oligomers. Such behavior has been observed, for example, with cyclopentene, cyclooctene, 1,5-cyclooctadiene, cyclododecene, and norbornene.[65] According to the simple pairwise mechanism, one would expect that the molecular weight of the product would gradually increase via cyclic oligomers of increasing size (as in condensation polymerization), and the relative proportions of the various cyclic oligomers would remarkably change. In fact, in the ROMP of 1,5-cyclooctadiene, a continuous series of cyclic oligomers $(C_4H_6)_n$ is formed, concurrently with high polymer. This was first noted in 1969 using $WCl_6/EtAlCl_2/EtOH$ as the catalyst and has since been observed with many other catalysts. This observation is difficult to explain in terms of the pairwise mechanism, but can be readily interpreted by the metal-carbene mechanism, in which the propagation reaction is in competition with the backbiting reaction.[96,97]

Final support for the metal carbene mechanism came from Casey and Burkhardt's work,[98] in which a metal carbene was isolated and showed metathesis reaction with an olefin. Katz *et al.*[99] extended Casey and Burkhardt's findings in 1976, when he demonstrated that the same carbene initiated the ring opening

polymerization of cyclooctene with incorporation of the initial alkylidene into the polymer chain.

Development of Lewis Acid-Free Metathesis Catalysts

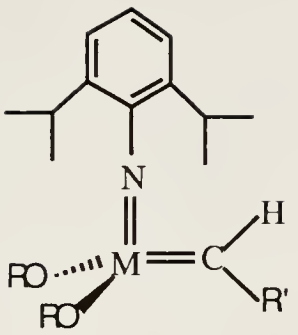
The metal carbene mechanism shows that the metal alkylidene moiety is the key structure responsible for the olefin metathesis reaction. This finding has directed researchers away from the poorly defined and less understood classical catalysts and towards the synthesis of well-defined transition metal alkylidene complexes that can directly catalyze the olefin metathesis reaction.

In classical metal catalyst systems, the metal complex reacts with a co-catalyst (usually a Lewis acid) to produce a metal alkylidene at the initial stage of the metathesis reaction. Well-defined metal carbene complexes, however, can directly catalyze olefin metathesis reaction without a Lewis acid co-catalyst. The early well-defined yet relatively inactive catalysts are known as Fischer-type carbene complexes and are characterized by the presence of heteroatoms (O, N, S) bonded to the carbene carbon, such as $(CO)_5Mo=C(OPh)Me$,[100] $(CO)_5W=C(OMe)Ph$,[101] $(CO)_4W=C(OMe)-(CH_2)_2CH=CH_2$.[102] Such Fischer carbene complexes do not normally initiate the olefin metathesis reaction because they are both coordinately and electronically (18 e) saturated. They can sometimes, however, be activated for metathesis by heating (e.g., $(CO)_5W=C(OMe)Ph$), or by reaction with a co-catalyst (e.g., $(CO)_5Mo=C(OPh)Me$ with $MeAlCl_2/Bu_4NCl$). These treatments remove one of the ligands, and the vacancy thus created at the metal site is

then available for coordination of an olefin and subsequent metathesis via the intermediate metallacyclobutane.

Since Fischer carbene complexes cannot initiate a metathesis reaction directly, chemists have searched for metal alkylidenes with both coordinately and electronically unsaturated structures that could directly catalyze the metathesis reaction. The first such carbene complex was obtained by Ofele,[103] and since then, a variety of synthetic routes for alkylidene complexes, $LnM=CR^1R^2$ (R^1, R^2=H, alkyl, aryl), have been discovered.[104] Some of these complexes are good initiators for exchange olefin metathesis and metathesis polymerization in absence of a Lewis acid. An example of such a complex is $W(=CHCMe_3)(OCH_2CMe_3)_2Br_2$,[105] formally a 12-electron species, which is readily able to coordinate with a substrate olefin prior to reaction. The complexes $W(=CHCMe_3)(NAr)(OR)_2$[106-108] (Ar=2,6-C_6H_3-i-Pr_2; OR=O-2,6-C_6H_3-i-Pr_2, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$) and $W(=CHCMe_3)(CH_2CMe_3)_2Cl$[109] are 4-coordinate, electron-deficient, and active for metathesis. The rhenium-carbene complex, $Re(=CHCMe_3)(NAr)_2(OR)$ (OR=O-2,6-C_6H_3-i-Pr_2, $OCH(CF_3)_2$),[110] which is also 4-coordinate, however, is inactive for metathesis reactions because it has an electron count of 18 (if the lone pairs on each nitrogen are counted).

Among well-defined, low coordinative, electron-deficient metal carbene complexes, the high oxidation and four coordinate Schrock's tungsten and molybdenum alkylidenes (Figure 1.17)[106,108,111,112] of the type $M(CHR')(NAr)(OR)_2$ (M=W, Mo; Ar=2,6-C_6H_3-i-Pr_2; R'=CMe_2Ph, t-Bu) are the most important metathesis catalysts due to their stability and high reactivity.



M	R'	No
W	t-Bu	1a
W	CMe_2Ph	1b
Mo	CMe_2Ph	1c

Figure 1.17 Highly reactive Lewis acid-free Schrock alkylidene.

The early work of metal carbene complexes suggests that the best catalytic metal alkylidene should have the highest possible oxidation state and lowest coordination number.[113] A 4-coordinate VIB transition metal (W, Mo) complex could only be obtained by using an oxo or imido ligand, of which the oxo was discarded because it could not provide any stabilizing steric bulk to the complex. An aromatic imido ligand, such as N-2,6-C_6H_3-i-Pr_2, has been used in Schrock's catalysts because it provides the necessary bulk that prevents deactivation of the catalyst through intermolecular dimerization.[114]

The activity of Schrock alkylidene W(CH-t-Bu)(NAr)$(OR)_2$ in the metathesis of olefins depends critically upon the nature of the substituent OR. For example, the tungsten complex in which OR=$OCCH_3(CF_3)_2$ is an active catalyst for the metathesis of ordinary olefins at a rate that may be as high as 10^3 turnovers/min at 25 °C in a hydrocarbon solvent, whereas analogous OR=(O-t-Bu) complexes do not react readily with internal olefins.[115] Experimental evidence indicates that the greater the electron withdrawing power

of the alkoxides, the more electrophilic the metal center, thus the more stable the metallacyclobutane formed in the metathesis reaction. The very highly electron withdrawing alkoxide ligands, $OR=O(CF_3)_2CF_2CF_2CF_3$, however, form a too stable and relatively unreactive metallacycle and, consequently, cause a low metathesis conversion. An explanation for the above reactivity change with the nature of OR groups is that the nucleophilic attack of the olefin to the metal to form a metallacyclobutane is a rate determining step in metathesis reaction.

The reactivity of Schrock's catalyst is also related to the alkylidene ligand size. The neopentylidene [$=CHC(CH_3)_3$] catalyst can be 100 times less reactive than the propylidene ($=CHCH_2CH_3$) analog, yet is more stable than its less bulky counterpart.[106] The ligands in the catalysts were optimally selected based on their contributions to activities and stabilities of the catalysts.

The X-ray studies of 4-coordinate complexes of the type $M(CHR')(NAr)(OR)_2$(M=W, Mo; Ar=2,6-C_6H_3-i-Pr_2; R'=CMe_2Ph, t-Bu) show them to be pseudotetrahedral complexes in which the alkylidene substituent lies in the N/W/C plane and points toward the imido nitrogen atom (syn rotamer). It has been suggested that syn and anti rotamers are both accessible (anti referring to the rotamer in which the alkylidene substituent points away from the imido nitrogen atom) and, in some cases, have been observed to interconvert with an activation barrier of about 15 kcal.[116] The metallacycle of $W[CH(Me_3Si)CHCH_2](NAr)[OCMe(CF_3)_2]_2$ has been isolated and shown to be approximately trigonal-bipyramidal (TBP) tungstacyclobutane complexes in which the WC_3 ring is located in

the equatorial plane. Square-pyramidal (ST) tungstacyclobutane is observable for the least active catalysts (OR=O-t-Bu).[117]

Schrock alkylidenes readily react with aldehyde, carbonyl, and ester groups through a Wittig-type reaction (Figure 1.18), forming a metal oxide and thus resulting in deactivation of the catalysts.[118]

Figure 1.18. Wittig-type reaction between Schrock alkylidene and aldehyde.

Molybdenum complexes appear to be more tolerant of functionalities than are tungsten complexes. The less electrophilic molybdenum catalysts demonstrate a lower metathetic activity but a higher selectivity which allowed numerous functional groups to be incorporated into ROMP polymers. For example, monomers, which contain ether, ester, amide, nitrile, and thioether, have been polymerized through ROMP techniques.[118] Molybdenum complexes, however, are more readily decomposed than are their tungsten analogs through a rearrangement of metallacyclobutane complexes by a β-hydride mechanism and by bimolecular coupling of alkylidene ligands, especially methylidenes.[119] As Figure 1.19 shows, Mo(CH-t-Bu)(NAr)[OCMe$(CF_3)_2$]$_2$ reacts with excess ethylene to give trigonal-bipyramidal Mo($CH_2CH_2CH_2$)(NAr)[OCMe$(CF_3)_2$]$_2$, which is allowed to decompose in the presence of excess ethylene and yields an unstable molybdenacyclopentane complex Mo(NAr)-[OCMe$(CF_3)_2$]$_2$(C_4H_8), quantitatively. Therefore, analogous molybdenum catalysts seem to have important advantages over

tungsten catalysts for polymerizing functionalized monomers,[111] but are also less stable in the presence of excess ethylene.[119]

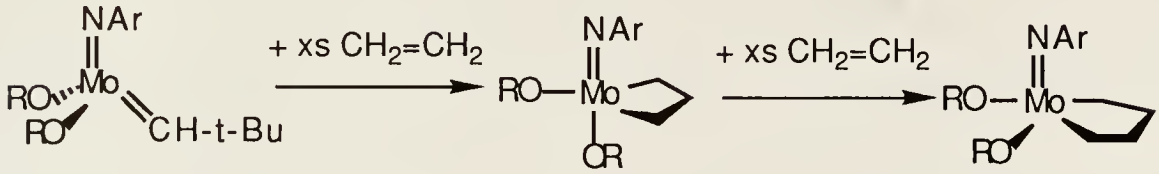


Figure 1.19. Decomposition of Mo catalyst in presence of excess ethylene.

Ring Opening Metathesis Polymerization (ROMP) and Acetylene Metathesis Polymerization

The first ring opening metathesis polymerization was conducted in 1957[65] and involved the metathesis reaction of cyclopentene and norbornene on MoO_3/Al_2O_3, which was activated with $LiAlH_4$ (Figure 1.20). This was followed by other academic and industrial research to look for new unsaturated polymers. Several commercial polymers have been produced by ring opening polymerization using classical catalysts. Trans-poly(norbornene) was the first commercial product prepared by the $RuCl_3$ catalyzed

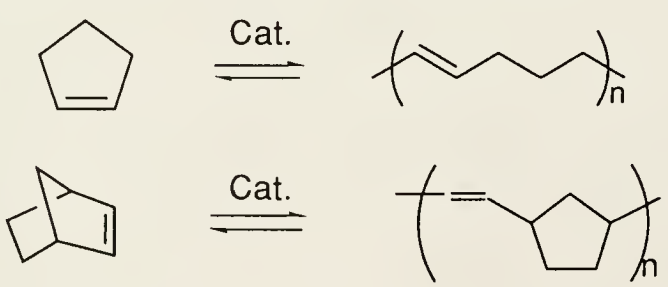


Figure 1.20. Ring opening metathesis polymerization of cyclopentene and norbornene.

polymerization of norbornene in 1976.[120] Next *trans*-poly(octenamer) was prepared by polymerization of cyclooctene.[121]

The polymerizability of a cyclic monomer greatly depends on ring strain. The strain is high for 3- and 4-membered rings because of the high degree of angle strain and is also high for 8-, 9-, and 10-membered rings because of the crowding strain of the rings. Ring strain for 5-, 6-, and 7-membered rings is low, and the sign of the free energy change (ΔG) for the polymerization process is sensitive to a number of physical factors: monomer concentration, temperature, and pressure. In very large rings containing negligible strain, the reaction is entropy driven through the gain of transitional entropy in the polymer.

There are two competitive reactions in ring opening metathesis polymerization: linear propagation producing a high molecular weight polymer and cyclization producing a series of cyclic oligomers. The mechanism for linear propagation in ROMP is shown in Figure 1.21, where the transition metal alkylidene

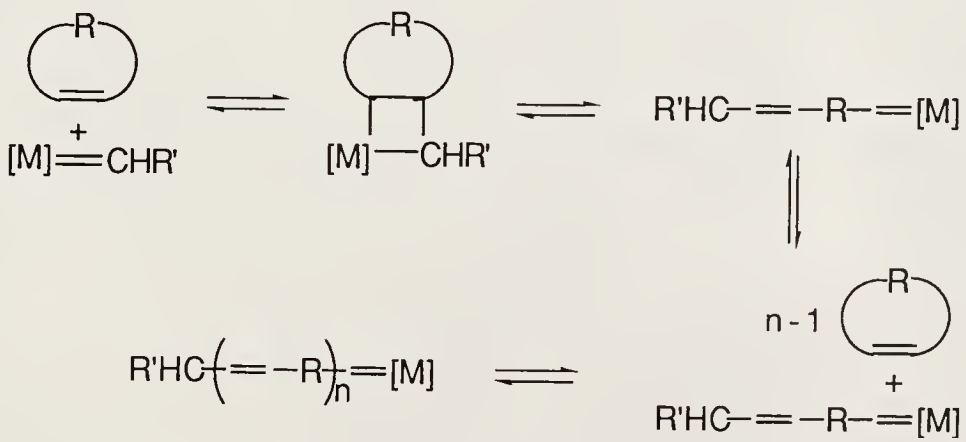


Figure 1.21. Mechanism for the ring opening metathesis polymerization.

(carbene), [M]=CHR', reacts with cycloalkene to form a metallacyclobutane intermediate. The metallacyclobutane then cleaves to produce a new metal alkylidene containing one repeat unit. The new metal alkylidene continues reacting with more cycloalkenes through the metallacyclobutane to form a high molecular weight polymer.

Cyclization happens through a backbiting intramolecular metathesis reaction, while chain propagation is proceeding (Figure 1.22). The formation of cycloalkene in ROMP is often observed, such as yielding cyclohexene in metathesis polymerization of 1,7-octadiene, 2,8-decadiene, and *cis, trans*-1,5-cyclodecadiene.[122]

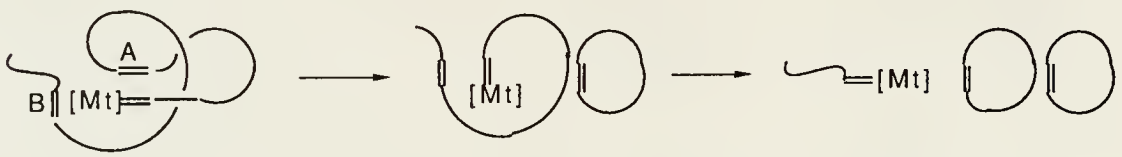


Figure 1.22. Formation of cyclic oligomers by intramolecular metathesis reaction.[123]

Ring opening metathesis polymerization is a "living" polymerization reaction, because the metal alkylidene remains attached to the growing end of the polymer chain (see Figure 1.22). "Living" refers to a nonterminated polymerization in which propagation species remain active in any reaction stage. The living polymerization produces polymers having a narrow molecular weight distribution (c.a. <1.1), and the molecular weight of the polymer depends on the ratio of monomer to initiator concentrations. Living polymerization offers a method to produce block copolymers of well defined structure by adding a second or even a third monomer in a

certain order.[124] A unique class of living polymerization catalysts for the ring opening metathesis polymerization are the highly active Lewis acid-free transition metal alkylidenes.[114,125-127]

The first living ring opening metathesis polymerization was reported by Grubbs and Tumas[125] in 1984 using titanacyclobutane complexes and norbornene (Figure 1.23). Schrock-type alkylidenes such as M(CH-t-Bu)(NAr)$(OR)_2$ (M=W, Mo)[114] are ideal for controlled living polymerization since they are relatively unreactive toward the acyclic C=C bonds along the polymer backbone, but are extremely reactive towards strained cyclic olefins, even at low temperatures.

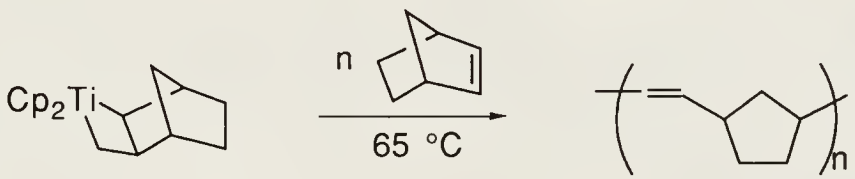


Figure 1.23. First living ring opening metathesis polymerization.

Ring opening metathesis polymerization is very useful in preparing polyacetylenes and its oligomers--polyenes through precursors or direct ring opening polymerization.[114,125,128-134] Feast[128] discovered that tricyclo[4,2,2,0]deca-3,7,9-triene and related molecules can be ring-opened by classical olefin metathesis catalysts to give a polymer from which an arene is ejected upon heating to produce polyacetylene (Figure 1.24). Knoll and Schrock[135] have reported the preparation of *tert*-butyl capped polyenes containing up to 15 double bonds, where polymerization of 7,8-bis(trifluoromethyl) tricyclo[4,2,2,0]deca-3,7,9-triene was

terminated by pivaldehyde in a Wittig-like reaction between the transition metal alkylidene and carbonyl group.

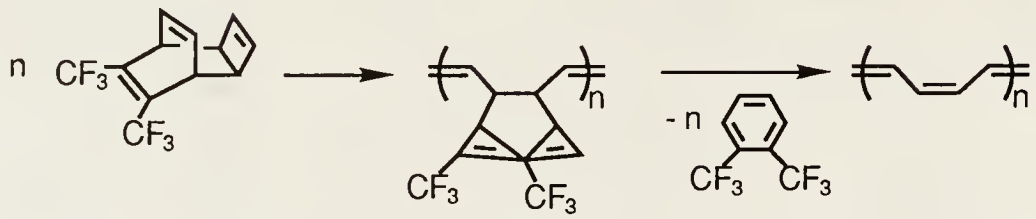


Figure 1.24. Preparation of polyacetylene from 7,8-bis (trifluoromethyl)tricyclo[4,2,2,0]deca-3,7,9-triene.

Polyacetylenes obtained from the metathesis polymerization of a substituted acetylene using transition metal catalysts have attracted a significant interest for chemists since the 1970s. The metathesis reactions of acetylene induced by metal carbene catalysts fall into three categories:[136-138] cyclotrimerization (Figure 1.25, (a)), polymerization (Figure 1.25, (b)) and exchange metathesis (Figure 1.25, (c)).

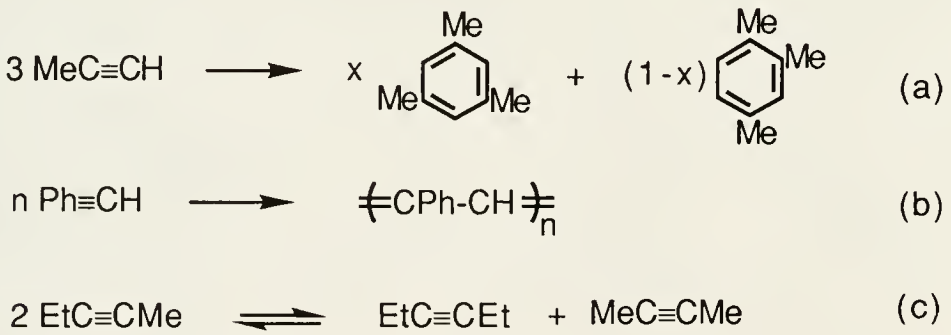


Figure 1.25. Three categories of acetylene metathesis reaction.

Both mono- and disubstituted acetylenes can form polyacetylene through catalyzed metathesis polymerization using classical metathesis catalysts or well-defined metal carbenes. In

the polymerization process, a metallacyclobutene is formed by combination of an alkylidene and acetylene triple bond, which is then cleaved to form a double bond adjacent to the alkylidene on the end of the chain (Figure 1.26).[65]

Poly(methylacetylene), poly(butylacetylene), and poly(phenyl acetylene) can be obtained through metathesis polymerization of corresponding monosubstituted acetylenes, using $RR'C{=}W(CO)_3$,

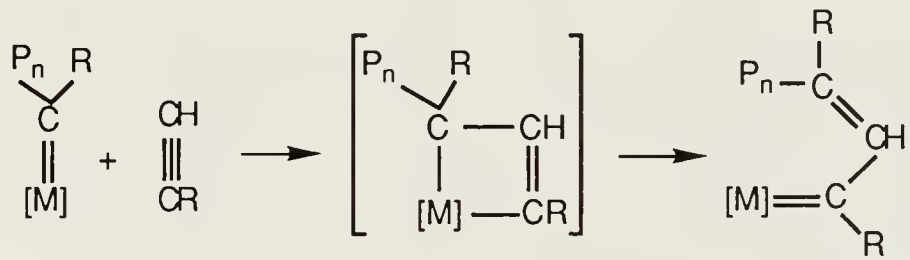


Figure 1.26. Propagation of polymerization of acetylene by a metal carbene chain carrier.

WCl_6/ROH, or $MoCl_5$ as catalysts.[139-141] Disubstituted polyacetylenes can be synthesized using catalysts such as $RR'C{=}W(CO)_3$ and WCl_6/Ph_4Sn.[142,143] Since the acetylene metathesis polymerization is a living polymerization, block copolymers can be readily produced by the controlled addition of monomers in a particular sequential order. Schlund *et al.*[144] reported a triblock copolymer was obtained when W(CH-t-Bu)(NAr)(O-t-Bu)$_2$ was treated with 50 equiv of norbornene, then 3-9 equiv of acetylene, and then 50 equiv of norbornene.

Acyclic Diene Metathesis (ADMET) Polymerization

One of the most significant successes in metathesis chemistry is the development of acyclic diene metathesis (ADMET) polymerization, which extends metathesis polymerization to a new area. Early metathesis polymerizations include ring opening metathesis polymerization (ROMP) and acetylene metathesis polymerization. The former is a very useful polymerization method and produces variety of unsaturated polymers, of which some have become commercial products. The latter is limited to obtaining only polyacetylenes and related copolymers. The new ADMET polymerization method has produced numerous different unsaturated polymers, many of which are difficult to obtain by any other method.

Acyclic diene metathesis polymerization is a step, condensation, equilibrium polymerization. This potential polymerization method was first attempted as early as 1970, but with little success.[145-147] Dall'Asta *et al.*[145] were the first to report the attempted polymerization of 1,5-hexadiene and 1,4-pentadiene using classic metal catalysts with Lewis acid as a co-catalyst. During the reaction, only linear unsaturated oligomers were obtained and ethylene was released. Other early attempts by Doyle[146] and Zuech *et al.*[147] further demonstrated that the classical Lewis acidic catalysts would not catalyze step polymerization to produce high molecular weight polymer.

In 1987, Lindmark-Hamberg and Wagener re-investigated the polymerization of 1,5-hexadiene using tungsten hexachloride/ethyl aluminum dichloride as the metathesis catalyst.[148] Again the

reaction produced low molecular weight metathesis polymers. Through a careful analysis of the reaction products, they discovered that vinyl addition competed with metathesis, leading to a mixture of products and failure to produce a high molecular weight metathesis polymer. The Lewis acid co-catalyst was responsible for a cationic chain propagation that produced vinyl addition products, including crosslinking polymer.

To obtain further evidence for competing reactions between vinyl addition and metathesis condensation polymerization, Wagener and co-workers designed and carried out two elegant model studies[149-150] using styrene and substituted styrenes as reagents and $WCl_6/EtAlCl_2$ as the catalyst. Only the cationic polymerization product, polystyrene, was obtained (Figure 1.27), which indicated that the catalyst used for the metathesis reaction catalyzes cationic vinyl addition reactions as well.

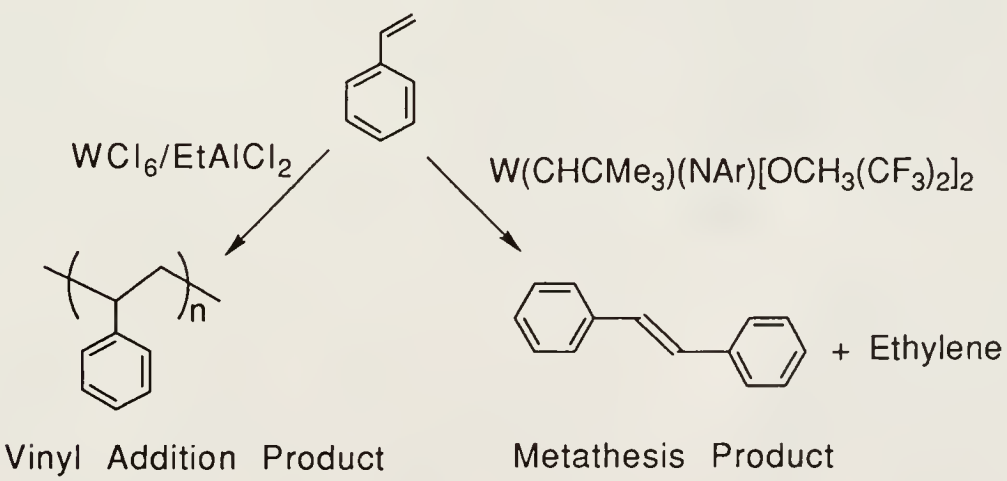


Figure 1.27. Model studies for cationic vinyl addition with classic Lewis acidic catalyst system and metathesis polymerization with Lewis acid-free catalyst system.

Step and chain addition polymerization have significantly different mechanisms basically in terms of the time-scale of various reaction events. Chain polymerization produces polymer molecules almost immediately after the reaction begins. Polymerization occurs by the propagation of the reactive species through the successive, rapid addition of large numbers of monomer molecules to a chain. Therefore, high molecular weight polymers are formed as soon as the polymerization has started.

Step polymerization proceeds by the stepwise reaction between the functional groups of reactants, and the size of the molecules increases at a relatively slow rate. Reaction proceeds slowly from monomer to dimer, trimer, tetramer, and so on until eventually large polymer molecules are formed. Therefore, monomers disappear at an early reaction stage, and high molecular weight molecules form at the final stage when reaching a very high monomer conversion. In small molecule synthesis the reaction is considered to be a success if 90% conversion is achieved. In contrast, a conversion of greater than 99% is needed for any step polymerization to produce a high molecular weight polymer. The relationship between conversion and degree of polymerization can be described by Carothers equation:[2]

$$\bar{X}_n = 1/(1-p)$$

where $\bar{X}_n$ is the number average degree of polymerization and p is the extent of conversion of the functional group. A plot of this equation (Figure 1.28) reveals the need for high conversion of monomer(> 99%) before a high molecular weight polymer is produced.

P	$\bar{X}$
0.8	5
0.9	10
0.95	20
0.99	100
0.995	200

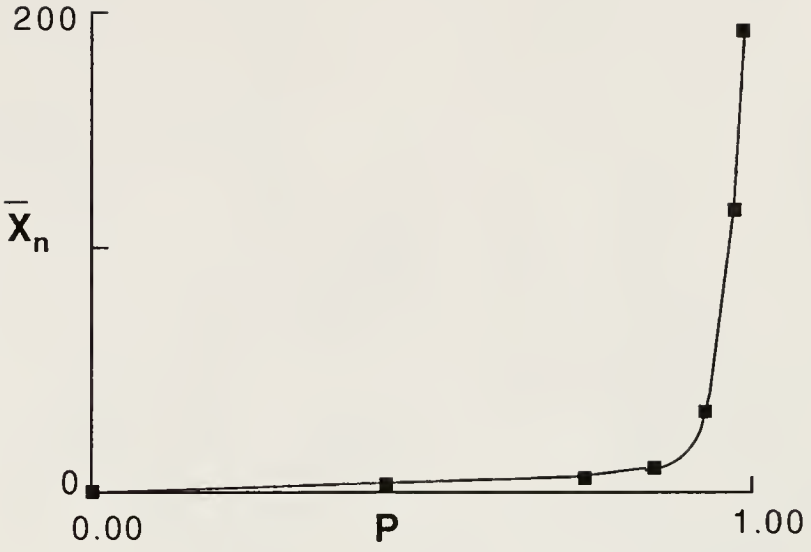


Figure 1.28. Variation of molecular weight with conversion for equilibrium step polymerization.

In ADMET polymerization, the need for high conversion of monomers is met by the elimination of vinyl addition reactions, which can be achieved by using Lewis acid-free metal alkylidenes as metathesis catalysts. In their model study of the metathesis reaction of styrene with Schrock's tungsten catalyst, Wagener and co-workers found that stilbene was the only resulting product and no trace of vinyl addition product was produced[149,150] (see Figure 1.27). Those model studies led the way to successful ADMET polymerization. The first high molecular weight polymer was produced by the ADMET polymerization of 1,9-decadiene to polyoctenamer, using tungsten catalyst W(CH-t-Bu)(N-2,6-C_6H_3-i-Pr_2)[OCME(CF_3)$_2$]$_2$.[149,150] Further research has demonstrated that a variety of unsaturated polymers, including those containing different functionalities, could be obtained through ADMET polymerization.

The mechanism of ADMET polymerization is shown in Figure 1.29, where the original alkylidene (e.g., neopentylidene) reacts with a terminal olefin, forming a metallacyclobutane (step 1), which is then cleaved to a monomer-type metallalkylidene and a small olefin molecule (step 2). Advancing clockwise, the monomer-type

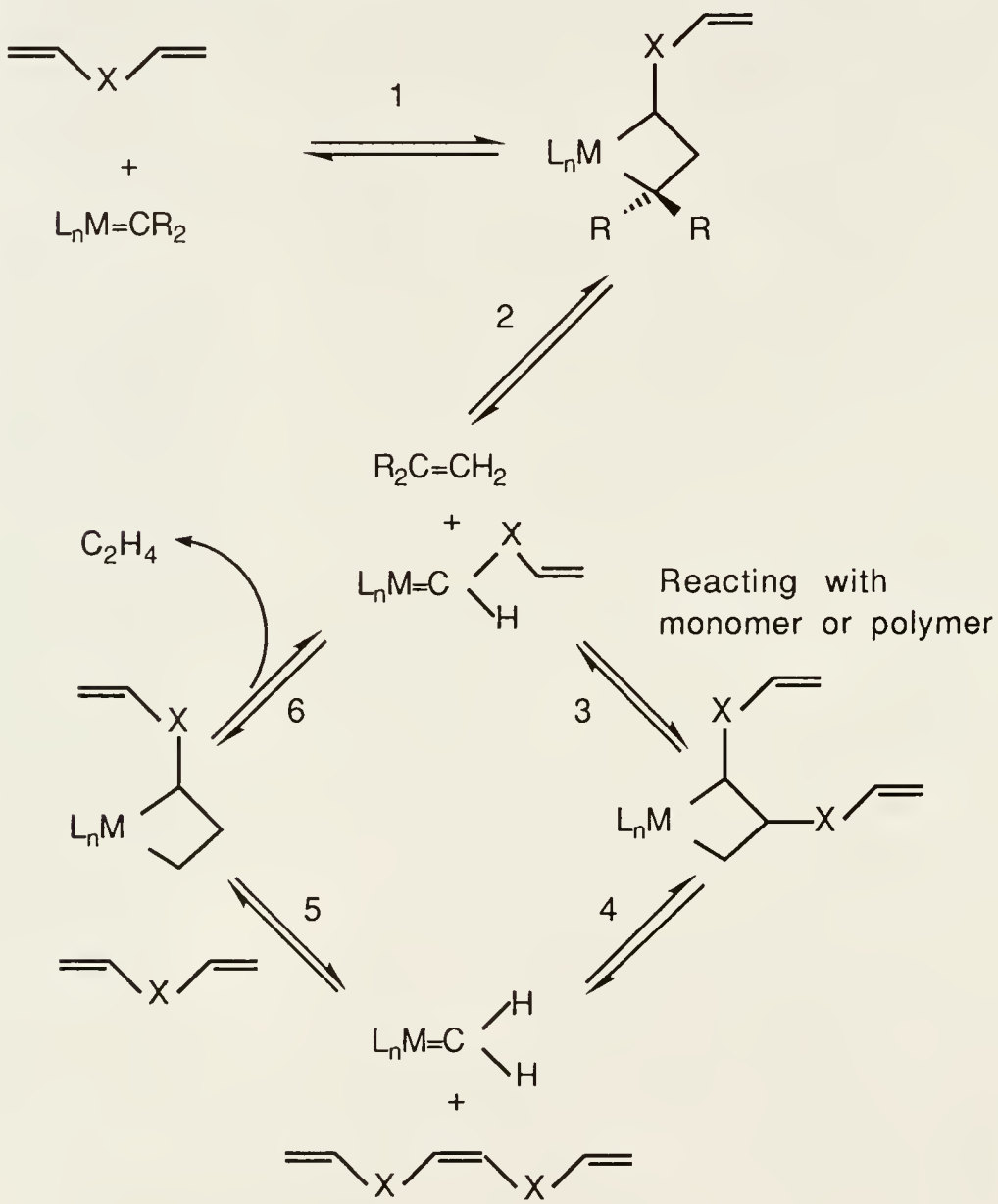


Figure 1.29. Scheme of ADMET polymerization.

metallalkylidene is reacted with a second monomer to form a dimer-type cyclobutane (step 3) and produces a dimer and metallamethylidene (step 4). Through the continuous cycle of steps of 3 to 6, the molecule chain grows to a high molecular weight polymer. Small molecules that are produced in the reaction are evacuated continuously to push this equilibrium polymerization forward.

While unsaturated polymers containing different functionalities have been produced using both tungsten and molybdenum catalysts, it has been found that the molybdenum based catalyst seems to be more tolerant to functionalized diene than its tungsten analog. Brzezinska and Wagener[151-153] discovered that a series of ether-containing dienes could be ADMET polymerized to ether-containing unsaturated polymers. Such ether-containing polymers can only be produced with the monomers, $CH_2=CH-(CH_2)_n-O-(CH_2)_n-CH=CH_2$, which have a number of methylene groups between oxygen and olefin equal to or greater than 2 ($n\geq 2$). Divinyl ether ($n=0$) and diallyl ether ($n=1$) do not polymerize via a metathesis reaction when catalyzed by a neopentylidene tungsten catalyst. Similar results are observed when using the molybdenum neopentylidene, except that, in this condition, polymerization of diallyl ether produced an equilibrium mixture of 2,5-dihydofuran and linear oligomers.[153]

Following this ether research, Wagener and co-workers [154-156] demonstrated that unsaturated polyesters, polycarbonates, and polyketones can be obtained through ADMET

polymerization of correspondent functionalized monomers. The unsaturated polycarbosilanes[157], polycarbosiloxanes[158] and sulfur containing polymers[159] have been synthesized by ADMET polymerization as well. Random copolymers containing octenylene and butenylene in a statistical array based on feed ratio have been obtained from copolymerization of 1,9-decadiene and 1,5-hexadiene.[160] The block poly(1,4-phenylenevinylene-co-octenamers) have been obtained through copolymerization of 1,4-dipropenylbenzene and 1,9-decadiene.[161]

Study on the Chemistry of Conjugated Monomers in ADMET Polymerization

Since successful ADMET polymerization was first achieved in 1988, a number of unsaturated polymers, such as ether, ester, ketone, carbonate, silane and thioether containing polymers, have been successfully synthesized from different monomers through this new polymerization method. This dissertation describes a study of the reactivities of conjugated monomers in ADMET polymerization in an effort to extend this polymerization area. The monomers used are those in which two olefins are directly conjugated together or conjugated by phenylene group. The polymers produced are polyacetylene, poly(phenylene vinylene), and their derivatives, which are potentially useful as conducting and nonlinear optical materials.

Different conjugated dienes are explored in this study. Polyacetylene oligomers are obtained by ADMET polymerization of

2,4-hexadiene and 2,4,6-octatriene in bulk and solution conditions. The reactivites of 1,3-butadiene and 1,3,5-hexatriene are examined. Copolymerization of 2,4-hexadiene and 2,10-dodecadiene is conducted at room temperature.

Telechelic polyacetylenes are synthesized through ADMET polymerization of 2,4-hexadiene with internal monoolefins. The ADMET polymerization and copolymerization of 1,2- and 1,3-dipropenylbenzene are conducted at room temperature using a molybdenum catalyst.

CHAPTER 2

EXPERIMENTAL

Instrumentation

Proton nuclear magnetic resonance (NMR) 200 MHz, ^{13}C nuclear magnetic resonance 50 MHz, and solid state carbon NMR spectra were obtained with a Varian XL-200 series NMR Surperconducting Spectrometer system. Chloroform-d ($CDCl_3$) or benzene-d_6, purchased from Aldrich, was directly used as the solvent without further purification. In NMR metathesis reaction, solvent benzene-d_6 was purified with calcium hydride and sodium mirror to eliminate moisture and oxygen. All proton chemical shifts were reported in parts per million down field from tetramethylsilane (TMS), and carbon chemical shifts reported were internally referenced to $CDCl_3$ or benzene-d_6. Quantitative ^{13}C NMR spectra were run for 8-12 h with a pulse delay of 10-20 sec. Ultraviolet analyses were performed on a Perkin-Elmer Lambda 9 UV/Vis/NIR spectrophotometer with a scanning rate of 60 nm/min and chloroform as solvent. Gas chromatography was carried on a Hewlett Packard 5880A series equipped with a FID detector and a fused silica 0.31 mm x 50 m capillary column packed with a 0.17 m film of SE-54 (methylphenylsilicone). Mass spectroscopy data were collected on a Finnigan 4500 Gas Chromatograph/Mass Spectrometer.

Elemental analyses of compounds were performed by Atlantic Microlab Inc. in Norcross, Georgia, or by the Department of Chemistry, University of Florida.

Gel permeation chromatography (GPC) was carried on a Waters Associates liquid chromatography apparatus equipped with a U6K injector and differential refractometor and a Perkin-Elmer LC-75 ultraviolet (UV) spectrophotometric detector. A set of two Phenomenex 7.8 mm x 30 cm crosslinked polystyrene-divinylbenzene columns, 100 Å and 500Å or 500 Å and 5000 Å, were used. The mobile phase was HPLC grade tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. The calibration curve for molecular weight calculation was obtained from polybutadiene standard samples (Polysciences, Inc.) with a molecular weight distribution smaller than 1.07. Polymer samples were dissolved in THF and filtered, then injected to examine the retention time. All data were collected and analyzed on a Zenith personal computer model 48 equipped with Metrabyte multi-IO card.

Reagents and Purification

Three different types of Lewis acid free metal catalysts were used in this study: $W(CHCMe_3)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCH_3(CF_3)_2]_2$ 1a; $W(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCH_3(CF_3)_2]_2$ 1b; $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCH_3(CF_3)_2]_2$ 1c (for structures of the catalysts, see page 20, Figure 1.17). These three catalysts were prepared according to published methods developed by Schrock *et al.*[106,112]

Since well-defined, Lewis acid-free metal catalysts are very sensitive to traces of moisture and oxygen, all reagents used in a metathesis reaction were carefully purified using the following procedures. The volatile liquid reagents were stirred over calcium hydride in a round bottom flask stoppered with a drying tube until no evolution of hydrogen gas was observed. This predried reagent was degassed by at least three freeze-thaw cycles on a high vacuum line, then transferred under vacuum to a sodium mirrored flask and stirred until reaction of impurities with sodium was no longer evident. After dryness and absence of oxygen were accomplished, the reagent was transferred to a vacuum flask and sealed with a Rotoflow™ valve. Reagents reacted with sodium, such as 4-pentene-1-yl acetate and 3-butenal diethyl acetal, were dried only through the calcium hydride procedure described above and carefully degassed via a minimum of five freeze-thaw cycles. Non-volatile liquid reagents were heated under high vacuum for removal of oxygen and moisture. Solid reagents were sublimed under vacuum line to ensure dryness and absence of oxygen.

n-Pentane was washed with concentrated sulfuric acid at least three times until there was no further coloration observed. It was then washed with 0.5 N $KMnO_4$ in 3 M H_2SO_4 three times, followed by aqueous $NaHCO_3$ and water several times to ensure the acid was rinsed out. The pentane was then dried over calcium hydride and distilled to a flask containing sodium potassium amalgam. This n-pentane was refluxed in ketyl under argon before distillation. Toluene was purified using a similar procedure described as n-pentane, but without being washed with 0.5 N $KMnO_4$

in 3 M H_2SO_4. Tetrahydrofuran and ether were dried by refluxing over sodium/potassium benzophenone ketyl and distilled under argon protection. Other solvents were reagent or HPLC grade and redistilled before use in the reaction.

General ADMET Reaction Techniques

All metathesis reactions and polymerizations were conducted on a customary ADMET apparatus,[149] which is a high vacuum (10^{-6} mm Hg) line system made in the glass shop at the University of Florida. This vacuum line was constructed entirely of Pyrex™ glass and consisted of a rotary oil pump in conjunction with an oil diffusion pump. High vacuum Pyrex™ ground glass joints were used at various junctions in the line to permit evacuation of reaction vessels and to transfer solvents and reagents from one vessel to another. The entire system was evacuated and dried thoroughly with a torch to remove traces of adsorbed water vapor and oxygen from the surface of the glass. The system then was checked for the presence of pinholes with a Tesla high voltage discharge coil. A 30 to 50 mL round bottom flask equipped with a high vacuum Rotoflow™ valve was used in all metathesis reactions and polymerizations. The reactions were conducted at a temperature range of 25 °C to 50 °C. A gas trap and a dry ice-isopropanol condenser were connected with a reaction flask so that ethylene or butene produced in the metathesis reaction could be collected and removed.

NMR Solution Reactions

In order to obtain intimate detail of the metathesis reactions, NMR solution reactions were performed in a NMR tube containing benzene-d_6, reagents, and catalysts. Generally, in an inert atmosphere, 30 mg of catalyst, Mo(CHCMe$_2$Ph)(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCCH$_3$(CF$_3$)$_2$]$_2$, was dissolved in 0.5 mL of benzene-d_6 in a NMR tube, and 20 to 50 mg of reagent was then added to the solution. The tube was sealed by the NMR cap. The reaction was then monitored by ^{1}H and ^{13}C NMR spectroscopy.

ADMET Polymerization of 2,4-Hexadiene 2

Monomer 2,4-hexadiene 2 was purchased from Aldrich Chemical Company, Inc. in 99% purity, which is a mixture of *trans,trans, trans,cis, and cis,cis* isomers.

Bulk Polymerization of 2,4-Hexadiene 2.

The polyacetylene oligomer 3a was synthesized through bulk ADMET polymerization of 2,4-hexadiene by the following procedure. In an argon-filled dry box, 1.0 g (12 mmol) of purified 2,4-hexadiene and 20 mg (0.025 mmol) of Schrock's tungsten catalyst 1a (mole ratio of monomer to catalyst, 490:1) were weighed and mixed in a round bottom flask. The reaction mixture was stirred, sealed, and then moved to a vacuum system. The polymerization was carried out at room temperature with stirring. The small molecular gases

generated from the reaction were removed by intermittent application of a high vacuum to drive the equilibrium reaction forward. The polyacetylene oligomer solid was formed in 5 min, and the reaction was continued for 12 h before quenching by exposure to air. The polymer was added to chloroform (swelling and partially soluble) and precipitated in methanol, then filtered and dried. It had the following yield and spectral properties:

yield		72%
Molecular weight	Integration of ^{1}H NMR	Mn=240, D.P.=8
	GPC	Mn=420, Mw=580, Mw/Mn=1.39
^{1}H NMR	(200 MHz, $CDCl_3$), δ	1.76 (d, 6 H, CH_3), 5.60-5.85 (br, 4 H, CH=CH), 6.0-6.5 (br, conjugated ene)
^{13}C NMR	(50 MHz, $CDCl_3$), δ	17.8, 17.9, 18.2, 18.6, 125.8, 126.3, 128.6, 129.3, 129.5, 129.6, 130.1, 130.4, 130.5, 130.6, 130.7, 130.8, 131.6, 131.8, 131.9, 132.2, 132.3, 132.5, 132.6, 132.8, 132.9, 133.1, 133.2, 133.3, 133.4, 133.5, 133.6, 133.7, 133.8, 133.9
UV (nm, $CHCl_3$)		290, 303, 317, 332, 349, 380, 404, 423

In order to collect and characterize the released 2-butene gas during metathesis polymerization, a NMR tube was connected to reaction flask. After enough gas was trapped by liquid nitrogen, the tube was removed and immediately filled with 0.5 mL of chloroform-d, then sealed with a NMR cap. The 2-butene was then characterized by ^{1}H and ^{13}C NMR spectroscopy. The NMR spectra showed 80% of *trans* isomer for the 2-butene produced. It had the following NMR spectra:

^{1}H NMR (200 MHz, C_6D_6), δ 1.51 (d, 6 H, CH_3 *cis*), 1.59 (d, 6 H, CH_3, *trans*), 5.39 (m, 2 H, -CH=CH-, *trans*), 5.48 (m, 2 H, -CH=CH-, *cis*)

^{13}C NMR (50 MHz, C_6D_6), δ 12.4 (CH_3 *cis*), 17.9 (CH_3, *trans*), 126.0 (-CH=CH-, *cis*), 127.6 (-CH=CH-, *trans*)

After the polyacetylene was precipitated out of the methanol, the remaining solids dissolved in methanol were obtained by evaporation of all solvents and then characterized by NMR spectroscopy. Low molecular weight polyacetylene and decomposed catalysts were found.

Solution Polymerization of 2,4-Hexadiene 2.

The polyacetylene oligomer 3b was synthesized through solution ADMET polymerization of 2,4-hexadiene 2 by the following procedure. In an argon-filled dry box, 20 mg of Schrock's tungsten catalyst 1a (0.025 mmol) and 10 mL of benzene were mixed in a 30 mL round bottom flask. The mixture was stirred until a uniform catalyst solution (2.5×10^{-3} M) was formed. The purified 2,4-hexadiene (1.0 g) was then added to the solution (1.2 M) and stirred immediately. Polyacetylene oligomers started to precipitate after 10 min. The reaction was conducted at room temperature for 12 h and then quenched by exposure to air. The polymer solution was subsequently added to the methanol, and polymer 3b precipitated, then was filtered, and dried. The polyacetylene oligomer 3b had the following yield and spectral properties.

Yield 74.3%

Molecular weight	Integration of ^{1}H NMR	Mn=420, D.P.=15
	GPC	Mn=540, Mw=800, Mw/Mn=1.47
^{1}H NMR	(200 MHz, $CDCl_3$), δ	1.76 (d, 6 H, CH_3), 5.60-5.85 (br, 4 H, CH=CH), 6.0-6.5 (br, conjugated ene)
UV (nm, $CHCl_3$)		364, 383, 406, 451, 470

Synthesis and Polymerization of 2,4,6-Octatriene 4

2,4,6-Octatriene was synthesized using the method reported in the literature.[162] Ethylmagnesium bromide (3.0 M in diethyl ether), DL-3-butyn-2-ol (99%), crotoaldehyde (99+%), and lithium aluminum hydride (powder, 95+%) were purchased from Aldrich Chemical Co.

Synthesis of Oct-6-ene-3-yne-2,5-diol 5

The 70 mL of 3.0 M of ethylmagnesium bromide in ether (0.21 mole) solution was added to a 500 mL three-neck round bottom flask filled with argon gas, and 200 mL of toluene was then added with stirring. The mixture was cooled to 0 °C while a solution of 3-butyn-2-ol (7.0 g, 0.10 mole) in ether was added; stirring was continued for 5 h at room temperature. After the mixture had been cooled to 0 °C, 7.7 g of crotoaldehyde (0.11 mole) in toluene (50 mL) were added, and the mixture was stirred for 6 h at room temperature; the original insoluble viscous complex then dissolved. Addition of an ammonium chloride aqueous solution, isolation of the organic solution, and distillation gave the oct-6-ene-3-yne-2,5-diol (10.6 g). It had the following yield and spectral properties:

Yield 75.6%

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.45 (d, 3 H, ((C-OH)-CH_3), 1.75 (d, 3 H, (=CH)-CH_3), 4.2-4.4 (br, 2 H, two -OH), 4.6 (m, 1 H, (OH)-CH-(CH_3)), 4.85 (d, 1 H, (=CH)-CH-(OH)), 5.5-5.7 (m, 1H, =CH-(CHOH)), 4.8-6.0 (m, 1 H, (CH_3)-CH=)

^{13}C NMR (50 MHz, $CDCl_3$), δ 17.4 (CH_3), 24.0 (CH_3), 57.9 (CH(OH)(C≡)), 62.4 (CH(OH)(C=)), 83.3 (≡C), 87.7 (C≡), 128.4 (CH=), 130.1 (=CH).

Synthesis of 2,4,6-Octatriene 4

In a 500 mL round bottom flask, 6.3 g (0.17 mole) of lithium aluminum hydride was dissolved in 300 mL of diethyl ether. The solution was then cooled down to 0 °C. A second solution of 7.8 g (0.055 mole) of oct-6-ene-3-yne-2,5-diol in diethyl ether was added dropwise into the above lithium aluminum hydride solution. After adding oct-6-ene-3-yne-2,5-diol, the whole mixture was heated at reflex temperature for 5 h. Addition of aqueous tartaric acid and evaporation of the dried ether layer gave a residue which was fraction distilled to give 2,4,6-octatriene (1.9 g). It had the following yield and spectral properties:

Yield 31.5%

^{1}H NMR (200 MHz, $CHCl_3$), δ 1.75 (dd, 6 H, CH_3), 5.4-5.8 (m, CH-=-CH, 2 H), 5.9-6.1 (m, CH-=-CH, 2 H), 6.2-6.6 (m, CH-=-CH 2 H)

^{13}C NMR (50 MHz, $CHCl_3$), δ 13.4 (CH_3, *cis*), 18.3 (CH_3, *trans*), 121.9, 124.6, 125.5, 125.7, 126.5, 127.1, 127.2, 127.3, 128.2, 128.7, 129.0, 129.5, 129.6, 129.7, 130.5, 131.8, 132.0, 132.6

UV (nm, $CHCl_3$) 261, 269, 279

Elemental Analysis: Calculated for C_8H_{12}: C, 88.82; H, 11.18
Found: C, 88.68, H, 11.23

Bulk Polymerization of 2,4,6-Octatriene 4

The polyacetylene oligomer 3c was synthesized through bulk ADMET polymerization of 2,4,6-octatriene 4. In an argon filled dry box, 1.0 g (9.3 mmol) of 2,4,6-octatriene and 20 mg (0.026 mmol) of Schrock's molybdenum catalyst 1c were weighed (mole ratio of monomer to catalyst, 350:1) and mixed in a round bottom flask. The reaction flask was stirred, sealed, and then moved to a vacuum system. The polymerization was carried on at room temperature with stirring. The small molecules generated from the reaction were removed by intermittent application of a vacuum. The polyacetylene solid 3c was formed in 5 min. The reaction was continued for 12 h and quenched by exposure to air. The polymer was dissolved in chloroform (swelling and partially soluble), precipitated in methanol, then filtered and dried. It had the following yield and spectral properties:

yield 69.4%

Molecular weight Integration of ^1H NMR Mn=280, D.P.=10
GPC Mn=360, Mw=670, Mw/Mn=1.72

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.75 (d, 6 H, CH_3), 5.55-5.80 (br, 4 H), 6.0-6.8 (br, conjugated ene)

^{13}C NMR (50 MHz, $CDCl_3$), δ 18.3 (CH_3, *trans*), 129.3, 129.8, 130.6, 130.7, 131.9, 132.0, 132.3, 132.4, 132.7, 132.8, 132.9, 132.8, 133.0, 133.2, 133.3, 133.4

UV (nm, $CHCl_3$) 290, 303, 317, 332, 349, 380, 404, 423

Attempted ADMET Polymerization of 1,3-Butadiene 6

Monomer 1,3-butadiene 6 was purchased from Aldrich Chemical Company, Inc. It was 99+% pure and was packaged in a steel cylinder. In order to eliminate any possible moisture and oxygen, monomer 6 was vacuum condensed into a sodium mirrored flask and sealed at room temperature for 2 h before use.

Attempted Bulk Polymerization of 1,3-Butadiene 6

A 25 mL Rotoflow™ valve-sealed reaction flask, containing 30 mg (0.039 mmol) of molybdenum catalyst 1c and a magnetic bar, was connected to a sodium-mirrored flask pre-stored with 1.0 gram of monomer 6 (18 mmol). This system was then set up to the vacuum line and the monomer 6 was vacuum transferred to the reaction flask. The reaction was conducted in this Rotoflow™ valve-sealed reaction flask at room temperature for 24 h. No polyacetylene polymer was observed. The unreacted monomer 6 was then transferred to a clean flask for further characterization, and the

solids remaining in the reaction flask were examined by ^{1}H and ^{13}C NMR spectroscopy.

The reaction was repeated for the reaction time of 5 min and 4 h.

NMR Reaction of 1,3-Butadiene and Molybdenum catalyst 1c

In an argon-filled dry box, 20 mg (0.37 mmol) of 1,3-butadiene, 30 mg (0.039 mmol) of molybdenum catalyst 1c, and 0.5 mL of C_6D_6 were mixed in a vial. The mixture was immediately transferred into a NMR tube and sealed, then characterized by ^{1}H and ^{13}C NMR spectroscopy at reaction times 0.5 h, 10 h, 36 h, and 9 days.

Attempted ADMET Polymerization of 1,3,5-Hexatriene 7

Monomer 1,3,5-hexatriene 7 was purchased from Aldrich Chemical Company, Inc., as 97% pure.

Attempted Bulk Polymerization of 1,3,5-Hexatriene 7

A same procedure for polymerization of 1,3-butadiene was followed. The reaction was conducted in a round bottom flask with a mixture of 1,3,5-hexatriene (1.0 g) and tungsten catalyst 1b (20 mg) for 24 h. A small portion of the monomer had reacted with catalyst. After evaporation of the unreacted monomer, the remaining solids were washed with methanol. An insoluble crosslinked polymer was obtained.

NMR Reaction of 1,3,5-Hexatriene and Molybdenum Catalyst 1c

The same procedure for the NMR reaction of 1,3-butadiene was followed, and 20 mg of 1,3,5-Hexatriene, 30 mg of molybdenum catalyst 1c, and 0.5 mL of C_6D_6 were used in this reaction. The solution was characterized by ^1H and ^{13}C NMR spectroscopy at reaction times: 0.5 h, 10 h, 36 h, and 56 h.

Synthesis and Polymerization of 2,10-Dodecadiene 9

Synthesis of 1,8-octylenebis(triphenylphosphonium bromide) 8

The 1,8-dibromooctane (98%) and triphenylphosphine (99%) were purchased from Aldrich Chemical Company, Inc., and used directly without further purification. A solution of 40.8 g (0.15 mole) of 1,8-dibromooctane and 86.5 g (0.33 mole) of triphenylphosphine in 400 mL of dimethylformamide was heated at reflex temperature with stirring for 3 h. The solution was then allowed to cool to room temperature and was slowly poured into diethyl ether with stirring. A white crystalline solid was precipitated from the solution and filtered, washed with ether, and dried on a vacuum line at room temperature. The dry weight of compound 8 was 117 g. It had following yield and spectral properties:

Yield 91.9%

^1H NMR (200 MHz, $CDCl_3$), δ 1.26-1.54 (br, 8 H, CH_2), 1.85 (m, 4 H, CH_2), 3.81 (t, 4 H, CH_2);

^{13}C NMR (50 MHz, $CDCl_3$), δ 28.0, 28.6, 32.7, 33.9

Synthesis of 2,10-Dodecadiene 9

Acetaldehyde (99%) and n-butyllithium (2.5 M solution in hexane) were purchased from Aldrich Chemical Company, Inc. In an argon purged 3-necked flask, 103 g (0.193 mole) of 1,8-octanylenebis(triphenylphosphonium bromide) 8 was added to 400 mL of dry THF. The mixture was cooled to -50 °C, and 154.1 mL of 2.5 M n-butyllithium (0.386 mole) was slowly added to the mixture to form ylide. The reaction was conducted at -50 °C for 30 minutes, over which time the solution changed from faint yellow to cherry red as the mixture was allowed to warm to room temperature. After 1 h at room temperature, the reaction mixture was cooled to -15 °C, and a THF solution of 17.83 g (0.405 mole) of acetaldehyde was added dropwise to the mixture over a period of 60 min, then heated at a slight reflux for 16 h. The reaction was quenched with aqueous NaHCO3 (5g/L), and extracted with ether. The ether layer was dried, and evaporated and the crude product was fractionally distilled. It had the following yield and spectral properties:

Yield 31.97%

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.23-1.51 (br, 8 H, CH_2), 1.64 (d, 6 H, CH_3), 2.04 (t, 4 H, CH_2), 5.41(m, 4 H, CH=CH)

^{13}C NMR (50 MHz, $CDCl_3$), *Trans* isomer: δ 17.8 (CH_3), 29.2 (CH_2), 29.6 (CH_2), 32.6 (CH_2), 124.5 (CH=), 131.6 (CH=);
Cis isomer: δ 12.6 (CH_3), 26.8 (CH_2), 29.1 (CH_2), 29.5 (CH_2), 123.5 (CH=), 130.8 (CH=)

Elemental Analysis: Calculated for $C_{12}H_{22}$: C, 86.67; H, 13.33
Found: C, 86.58; H, 13.38

Polymerization of 2,10-Dodecadiene 9

Methyl-terminated poly(octenamer) 10 was obtained through ADMET polymerization of 2,10-Dodecadiene 9. In an argon-filled dry box, 0.5 g (3.0 mmol) of compound 9 and 10 mg (0.013 mmol) of molybdenum catalyst 1c was added to a reaction flask, which was then set up on the vacuum line. The reaction was conducted with stirring at 30 °C until the reaction mixture solidified (24 h). The solid polymer was then dissolved in chloroform and precipitated in methanol. The white powder of methyl-terminated poly(octenamer) 10 was obtained. It had the following yield and spectral properties:

Yield 81.4%

Molecular weight Integration of ^{1}H NMR Mn=2810

GPC Mn=2450, Mw=3190, Mw/Mn=1.31

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.30(br, 8 H, CH_2), 1.63 (d, 6 H, CH_3), 1.96 (br, 4 H, CH_2), 5.37 (t, 4 H, CH=CH)

^{13}C NMR (50 MHz, $CDCl_3$), δ 18.3 (CH_3), 27.6, 29.4, 29.6, 30.0, 30.1, 33.0, 124.9, 130.3, 130.7, 132.0

Syntheses of Poly(acetylene-co-octenamers)

Attempted Copolymerization of 2,4-Hexadiene and 1,9-Decadiene 11

The 1,9-decadiene 11 was purchased from Aldrich Chemical Company, Inc, as 98% pure and was dried over calcium hydride and a sodium mirror. In an argon-filled dry box, 0.627 g (4.54 mmol) of 1,9-decadiene, 0.372 g (4.54 mmol) of 2,4-hexadiene, and 20 mg

(0.023 mmol) of catalyst 1b were mixed in a round bottom flask. The reaction was conducted on a vacuum line at room temperature with stirring. The metathesis reaction (bubbling) was observed initially and stopped gradually in 30 min. After 24 h, another 20 mg of catalyst was added. Again metathesis reaction was observed and gradually stopped in 30 min. After a total of 48 hours, the unreacted monomers were evaporated and the remaining solid was characterized by NMR spectroscopy. Only poly(octenamer) oligomer was found.

Synthesis of Poly(acetylene-co-octenamer) 1:1 Ratio 12

In an argon-filled dry box, 0.16 g (2.0 mmol) of 2,4-hexadiene and 0.33 g (2.0 mmol) of 2,10-dodecadiene were mixed in a 4 mL vial. The mixture was then added to a 30 mL round bottom reaction flask, which contained 20 mg (0.026 mmol) of molybdenum catalyst 1c. The reaction flask was then sealed and moved to a vacuum line. Polymerization was carried out at 30 °C with stirring, and the 2-butene generated in the reaction was removed by intermittent application of a vacuum. After the reaction mixture was completely solidified, the copolymer was dissolved in chloroform, precipitated in methanol, and then filtered and dried by a vacuum. It had the following yield and spectral properties:

Yield	70.3%	
Molecular weight	Integration of ^{1}H NMR	Mn=1090
	GPC	Mn=1090, Mw=1440, Mw/Mn=1.31

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.20-1.55 (br, CH_2), 1.63 (d, CH_3) 1.76 (d, CH_3), 1.88-2.27, (m, CH_2), 5.38 (m, nonconj., CH=CH), 5.48-5.82 (m, conj. CH=CH), 5.93-6.45, (m, conj. CH=CH)

^{13}C NMR (50 MHz, $CDCl_3$), δ 18.1, 27.4, 29.2, 29.5, 29.6, 29.8, 32.8, 33.0, 33.1, 124.7, 130.1, 130.6, 130.8, 131.0, 131.9, 132.6, 132.7, 133.2, 134.7, 135.3, 135.4

UV (CHCl3, nm) 239, 248, 273, 284, 305, 320, 335, 353, 382, 408, 431

Synthesis of Poly(acetylene-co-octenamer) 1:2 Ratio 13

In this synthesis, the same procedure for the 1:1 ratio copolymerization was followed. The mole ratio of 2,4-hexadiene (0.092 g) to 2,10-dodecadiene (0.365 g) was 1:2. The copolymer 13 had the following yield and spectral properties:

Yield 69.9%

Molecular weight Integration of ^{1}H NMR Mn=1510

GPC Mn=1420, Mw=2140, Mw/Mn=1.50

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.22-1.52 (br, CH_2), 1.64 (d, CH_3) 1.76 (d, CH_3), 1.88-2.27, (m, CH_2), 5.39 (m, ,internal CH=CH) 5.48-5.80, (m, conj. CH=), 5.92-6.30, (m, conj. CH=)

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.1, 27.4, 27.8, 29.2, 29.6, 29.8, 32.8, 33.0, 33.1, 125.8, 128.8, 130.1, 130.3, 130.5, 130.8, 131.0, 131.9, 132.6, 133.2, 134.7, 135.3, 135.4

UV (CHCl3, nm) 238, 273, 284, 305, 320, 381, 406

Synthesis of Poly(acetylene-co-octenamer) 1:4 Ratio 14

In this synthesis, the same procedure for the 1:1 ratio copolymerization was followed. The mole ratio of 2,4-hexadiene (0.052 g) to 2,10-dodecadiene (0.421 g) was 1:4. The copolymer 14 had the following yield and spectral properties:

Yield	68.9%	
Molecular weight	Integration of ^{1}H NMR	Mn=1340
	GPC	Mn=1580, Mw=2450, Mw/Mn=1.55
^{1}H NMR	(200 MHz, $CDCl_3$), δ	1.22-1.52 (br, CH_2), 1.64 (d, CH_3) 1.76 (d, CH_3), 1.88-2.27, (m, CH_2), 5.39 (m, internal CH=CH) 5.48-5.82, (m, conj. CH=CH), 5.93-6.28, (m, conj. CH=CH)
^{13}C NMR	(50 MHz, $CDCl_3$), δ	17.9, 29.0, 29.3, 29.4, 29.6, 32.6, 32.8, 124.5, 130.3, 130.8, 131.6, 132.4
UV ($CHCl_3$, nm)	236, 272, 283, 305, 320, 335, 353, 383, 408	

Synthesis of Poly(acetylene-co-octenamer) 2:1 Ratio 15

In this synthesis, the same procedure for the 1:1 ratio copolymerization was followed. The mole ratio of 2,4-hexadiene (0.230 g) to 2,10-dodecadiene (0.232 g) was 2:1. The copolymer had the following yield and spectral properties:

Yield	66.4%	
Molecular weight	Integration of ^{1}H NMR	Mn=730
	GPC	Mn=560, Mw=660, Mw/Mn=1.18

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.14-1.49 (br, CH_2), 1.63 (d, CH_3) 1.78 (d, CH_3), 1.83-2.18, (m, CH_2), 5.38 (br, internal CH=CH) 5.48-5.88, (m, conj. CH=CH), 5.93-6.45, (m, conj. CH=CH)

UV (CHCl3, nm) 236, 273, 283, 305, 320, 333, 352, 382, 406

Synthesis of Poly(acetylene-co-octenamer) 4:1 Ratio 16

In this synthesis, the same procedure for the 1:1 ratio copolymerization was followed. The mole ratio of 2,4-hexadiene (0.328 g) to 2,10-dodecadiene (0.166 g) was 4:1. The copolymer 16 had the following yield and spectral properties:

Yield 62.6%

Molecular weight Integration of ^{1}H NMR 540

GPC Mn=530, Mw=660, Mw/Mn=1.25

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.10-1.51 (br, CH_2), 1.63 (d, CH_3) 1.78 (d, CH_3), 1.86-2.26, (m, CH_2), 5.38 (br, internal CH=CH) 5.46-5.82, (m, conj. CH=CH), 5.82-6.50, (m, conj. CH=CH)

UV (CHCl3, nm) 274, 284, 305, 320, 332, 352, 380, 406

Attempted Polymerization of *cis,cis*-1,4-Dicyano-1,3-butadiene 17

Cis,cis-1,4-dicyano-1,3-butadiene (muconontrile) 17 was purchased from Aldrich Chemical Company, Inc., as 98% pure. It is a white crystalline solid (mp, 128-131 °C).

Attempted Solution Polymerization of *cis,cis*-1,4-Dicyano-1,3-butadiene 17

Compound 17 (0.104 g) was added into a 50 mL round bottom flask and sublimed by heating under a vacuum to remove moisture and oxygen. The flask was then moved into a dry box, and 10 mL of benzene and 20 mg of catalyst 1c were added to the flask. After 48 h of reaction at room temperature with stirring, benzene was evaporated and the remaining solids were characterized by NMR spectroscopy. The unreacted monomer 17 was found in the remaining solids, without observing polymers.

NMR Reaction of *cis,cis*-1,4-Dicyano-1,3-butadiene 17

In an argon-filled dry box, 30 mg of *cis,cis*-1,4-dicyano-1,3-butadiene (purified by sublimation) was dissolved in 0.5 mL of C_6D_6 in a vial, and 30 mg of molybdenum catalyst 1c was then added to this solution and stirred. The solution was immediately transferred to a NMR tube and characterized by NMR spectroscopy at reaction time 10 min, 30 min, 1 h, 2 h, 4 h, 6 h, and 16 h.

Attempted Polymerization of *trans,trans*-1,4-Diphenyl-1,3-butadiene 18

The *trans,trans*-1,4-diphenyl-1,3-butadiene (mucononitrile) 18 was purchased from Matheson Coleman & Bell, as 98% pure. It is a white crystalline solid (mp, 148-149 °C).

Attempted Solution Polymerization of *trans,trans*-1,4-Diphenyl-1,3-butadiene 18

In this reaction, the same procedure used for solution polymerization of *cis,cis*-1,4-dicyano-1,3-butadiene 17 was followed. The unreacted monomer 18 was found in the remaining solids, without observing polymers.

NMR Reaction of *trans,trans*-1,4-Diphenyl-1,3-butadiene 18

In this reaction, the same procedure used for NMR reaction of *cis,cis*-1,4-dicyano-1,3-butadiene 17 was followed. The reaction was characterized by NMR spectroscopy at reaction times 10 min, 30 min, 1 h, 2 h, 4 h, 6 h, and 16 h.

Synthesis of Isobutyl-Terminated Polyoctenamer 20

Telechelic polyoctenamer 20 was obtained through ADMET polymerization of 1,9-decadiene and a terminal monoolefin, 4-methyl-1-pentene 19 (Aldrich Chemical Company, Inc., 98% pure).

In an argon-filled dry box, 0.690 g (5.00 mmol) of 1,9-decadiene, 0.082 g (1.00 mmol) of 4-methyl-1-pentene, and 10 mg (0.012 mmol) of tungsten catalyst 1b were mixed in a round bottom reaction flask. The reaction was then conducted with stirring at room temperature for 48 h, and the ethylene generated in the reaction was removed by intermittent application of a vacuum. The solid product was dissolved in chloroform, precipitated in methanol,

filtered, and then dried under a vacuum. It had the following yield and spectral properties:

Yield 54.9%

Molecular weight Integration of ^1H NMR Mn=1240

^1H NMR (200 MHz, $CDCl_3$), δ 0.87 (d, 6 H, CH_3), 1.2-1.4 (br, 8 H, CH_2), 1.59 (m, 2 H, CH), 1.81-2.10 (br, 4 H, CH_2), 5.38 (m, 2H, internal olefin)

^{13}C NMR (50 MHz, $CDCl_3$), δ 22.3, 28.5, 27.2, 29.0, 29.6, 32.6, 36.4, 42.0, 128.9, 130.3, 131.5

Attempted Polymerization of 2,4-Hexadiene 2 with 4-Methyl-1-pentene 19

Attempted Bulk Polymerization of 2,4-Hexadiene with 4-Methyl-1-pentene

Bulk polymerization of 2,4-hexadiene with monoolefin 4-methyl-1-pentene was conducted in order to obtain isopropyl-capped polyacetylene. In an argon-filled dry box, 0.656 g (8.00 mmol) of 2,4-hexadiene, 0.336 (4.00 mmol) of 4-methyl-1-pentene, and 20 mg (0.026 mmol) molybdenum catalyst 1c were mixed together in a round bottom flask. The reaction was conducted with stirring at room temperature on a vacuum line. After 64 h, the liquid (mainly containing unreacted monomers) was evaporated and characterized by NMR spectroscopy and GC/mass spectrometer. The remaining solids were examined by NMR spectroscopy.

NMR Reaction of 2,4-Hexadiene and 4-Methyl-1-pentene with Molybdenum Catalyst 1c

The regular procedure for the NMR reaction was followed in this reaction. The 2,4-hexadiene (0.220 mmol), 4-methyl-1-pentene (0.430 mmol), molybdenum catalyst 1c (0.039 mmol), and benzene-d_6 (0.500 mL) were mixed in a NMR tube, which was then sealed and monitored by NMR spectroscopy at reaction times 15 min, 30 min, 60 min, and 24 h.

Metathesis Coupling Reaction of Functionalized Terminal Olefins

Attempted Metathesis Coupling of Allyl Chloride 21

Allyl chloride 21 was purchased from Aldrich Chemical Company, Inc., as 99% pure. In an argon-filled dry box, 1.0 g (13 mmol) of allyl chloride and 20 mg (0.026 mmol) of molybdenum catalyst 1c were mixed in a round bottom reaction flask. The reaction was conducted at room temperature with stirring on a vacuum line. After 48 h of stirring, the solution was characterized by NMR spectroscopy, which showed no coupling product.

Attempted Metathesis Coupling of Allyl Amine 22

Allyl amine 22 was purchased from Aldrich Chemical Company, Inc., as 99% pure. The same procedure for the coupling reaction of allyl chloride was followed, and 1.00 g (17.5 mmol) of allyl amine

and 20.0 mg (0.026 mmol) of molybdenum catalyst 1c were used. After 48 h of stirring, compound 22 remained unreacted.

Attempted Metathesis Coupling of 3-Butenal Diether Acetal 23

3-Butenal diether acetal 23 was purchased from Aldrich Chemical Company, Inc., as 97% pure. The same procedure for the coupling reaction of allyl chloride was followed, and 1.0 g (6.9 mmol) of allyl amine and 20 mg (0.026 mmol) of molybdenum catalyst 1c were used. After 48 h of stirring, the compound 23 remained unreacted.

Attempted Metathesis Coupling of 5-Hexen-2-one 24

5-Hexen-2-one 24 was purchased from Aldrich Chemical Company, Inc., as 98% pure. The same procedure for the allyl bromide reaction was followed, and 1.0 grams (10 mmol) of allyl amine and 20 mg (0.026 mmol) of molybdenum catalyst 1c were used. After 48 h of stirring, the compound 24 remained unreacted.

Metathesis Coupling of 4-Methyl-1-pentene 19

The compound 2,7-dimethyl-4-octene 26 was obtained through the metathesis coupling reaction of 4-methyl-1-pentane 19. In an argon filled dry box, 1.0 g (12 mmol) of compound 19 and 20 mg (0.026 mmol) of molybdenum catalyst 1c were mixed in a round bottom reaction flask. The flask was then moved to a vacuum line, and the reaction was conducted at room temperature with stirring for 48 h. The product 26 was vacuum distilled to a store flask and

characterized by NMR spectroscopy. It had the following yield and spectral properties:

Yield 99%

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (d, 12 H, CH_3), 1.59 (m, 2 H, CH), 1.88 (t, 4 H, CH_2), 5.36 (t, 2 H, CH=CH)

^{13}C NMR (50 MHz, $CDCl_3$) δ 22.3 (CH_3), 22.4 (CH_3), 28.5 (CH, *trans*), 28.7 (CH, *cis*), 36.4 (CH_2, *cis*), 42.1 (CH_2, *trans*), 129.2 (CH=, cis) 130.2 (CH=, *trans*)

Elemental Analysis: Calculated for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.45; H, 14.34.

Metathesis Coupling of 4-Penten-1-yl-acetate 27

Compound 4-octen-1,8-diyl acetate 28 was synthesized through the metathesis coupling reaction of 4-penten-1-yl acetate 27, which was purchased from Aldrich Chemical Company, Inc., as 98% pure. The same procedure for the coupling reaction of 4-methyl-1-pentene was followed, and 1.0 g (7.8 mmol) of compound 27 and 20 mg (0.026 mmol) of molybdenum catalyst 1c were used in this reaction. The product 28 had the following yield and spectral properties:

Yield 99%

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.68 (m, 4 H, CH_2), 1.98-2.18 (br, 10 H, CH_2 and CH_3), 4.05 (t, 4 H, CH_2), 5.42 (m, 2 H, internal CH=CH)

^{13}C NMR (50 MHz, $CDCl_3$) δ 20.8 (CH_3), 23.4 (CH_2), 28.4 (CH_2, *trans*), 28.7 (CH_2, *cis*), 63.8 (CH_2), 129.3 (CH=, *cis*), 129.77 (CH=, *trans*), 171.0 (C=O)

Elemental Analysis: Calculated for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83
Found: C, 63.08; H, 8.91

Metathesis Coupling of Allyltrimethylsilane 29

Compound 1,4-bis(trimethylsilyl)-2-butene 30 was synthesized through the metathesis coupling reaction of allyltrimethylsilane 29, which was purchased from Aldrich Chemical Company, Inc., as 99% pure. The same procedure for the coupling reaction of 4-methyl-1-pentene was followed, and 1.0 g (8.8 mmol) of compound 29 and 20 mg (0.026 mmol) of molybdenum catalyst 1c were used in this reaction. The product 30 had the following yield and spectral properties:

Yield 99%

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.01 (t, 18 H, CH_3), 1.41 (m, 4 H CH_2), 5.23 (m, 2 H, CH=CH, *trans*), 5.32 (m, 2 H, CH=CH, *cis*)

^{13}C NMR (50 MHz, $CDCl_3$) δ 1.97 (CH_3), 1.98 (CH_3), 17.8 (CH_2, *cis*), 22.7 (CH_2, *trans*), 123.1 (CH=, *cis*), 124.3 (CH=, *trans*)

Elemental Analysis: Calculated for $C_{10}H_{24}Si_2$: C, 59.91; H, 12.07
Found: C, 59.90; H, 12.18

Syntheses of Telechelic Polyacetylenes

Synthesis of Hexyl-Terminated Polyacetylene 32

Telechelic polyacetylene 32 was synthesized through ADMET polymerization of 2,4-hexadiene with *trans*-7-tetradecadiene 31 (Aldrich Chemical Company, Inc., 98% pure). In an argon-filled dry box, 0.328 g (4.00 mmol) of 2,4-hexadiene, 0.196 g (1.00 mmol) of *trans*-7-tetradecadiene, and 20 mg (0.026 mmol) of molybdenum catalyst 1c were mixed in a round bottom flask. The flask was then moved to a vacuum line, and the butene generated in the reaction was removed by intermittent application of a vacuum. The reaction was conducted at room temperature for 36 h. The product 32 was dissolved in chloroform, precipitated in methanol, and dried under a vacuum. It had the following yield and spectral properties:

Yield	68.8%	
Functionality	1.9	
Molecular weight	Integration of ^{1}H NMR	Mn=330, DP=6
	GPC	Mn=340, Mw=650, Mw/Mn=1.94

^{1}H NMR (200 MHz, $CDCl_3$), δ 0.88 (t, 6 H, CH_3), 1.21-1.48 (br, 12 H, CH_2), 1.68 (br, 4 H, CH_2), 2.08 (m, 4 H, CH_2 next to conj. CH=CH), 5.62-6.55 (br, conj. CH=CH).

Synthesis of Isobutyl-Terminated Polyacetylene 33

Telechelic polyacetylene 33 was synthesized through ADMET polymerization of 2,4-hexadiene with 2,7-dimethyl-4-octene 26. The same procedure for the synthesis of telechelic polyacetylene 32

was followed, and 0.328 g (4.00 mmol) of 2,4-hexadiene and 0.140 g (1.00 mmol) of 2,7-dimethyl-4-octene were used in the reaction. The product 33 had the following yield and properties:

Yield 59.6%

Functionality 1.6

Molecular weight Integration of ^{1}H NMR Mn=290, DP=7

GPC Mn=790, Mw=1590, Mw/Mn=2.01

^{1}H NMR (200 MHz, $CDCl_3$), δ 0.89 (d, 12 H, CH_3), 1.65 (m, 2 H, CH), 2.00 (t, 4 H, CH_2), 5.62-6.40 (br, conj. CH=CH)

Synthesis of Phenyl-Terminated Polyacetylene 35

Telechelic polyacetylene 35 was synthesized through ADMET polymerization of 2,4-hexadiene with propenylbenzene 34. The same procedure for the synthesis of telechelic polyacetylene 32 was followed, and 0.328 g (4.00 mmol) of 2,4-hexadiene and 0.236 g (2.00 mmol) of propenylbenzene were used in the reaction. The product 35 had the following yield and spectral properties:

Yield 63.4%

Functionality 1.4

Molecular weight Integration of ^{1}H NMR Mn=340, DP=7

GPC Mn=730, Mw=1250, Mw/Mn=1.72

^{1}H NMR (200 MHz, $CDCl_3$), δ 5.98-6.65 (br, conj. CH=CH), 6.65-6.95 (m, 2H, =CH-Ph), 7.16-7.55 (m, 10 H, phenyl)

Synthesis of Trimethylsilyl Methylene-Terminated Polyacetylene 36

Telechelic polyacetylene 36 was synthesized through ADMET polymerization of 2,4-hexadiene with 1,4-bis(trimethylsilyl-2-butene) 30. The same procedure for the synthesis of telechelic polyacetylene 32 was followed, and 0.328 g (4.00 mmol) of 2,4-hexadiene and 0.200 g (1.00 mmol) of 1,4-bis(trimethylsilyl-2-butene) were used in the reaction. The product 36 had the following yield and spectral properties:

Yield	57.4%	
Functionality	1.3	
Molecular weight	Integration of ^{1}H NMR	Mn=410, DP=9
	GPC	Mn=560, Mw=840, Mw/Mn=1.49
^{1}H NMR	(200 MHz, $CDCl_3$), δ	0.2-0.8 (m 18 H, CH_3), 1.35 (m, 4 H, CH_2), 5.65-6.50 (br, conj. CH=CH)

Synthesis of 3-yl-Acetate-propyl-Terminated Polyacetylene 37

Telechelic polyacetylene 37 was synthesized through ADMET polymerization of 2,4-hexadiene with 4-Octen-1,8-diyl acetate 28. The same procedure for the synthesis of telechelic polyacetylene 32 was followed, and 0.328 g (4.00 mmol) of 2,4-hexadiene and 0.204 g (1.00 mmol) of 4-Octen-1,8-diyl acetate were used in the reaction. The product 37 had the following yield and spectral properties:

Yield	55.4%	
Functionality	1.3	
Molecular weight	Integration of ^{1}H NMR	Mn=310, DP=5

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.64 (m 4 H, CH_2), 2.05 (s, 6 H, CH_3), 2.2 (m, 4 H, CH_2), 5.60-6.40 (br, conj. CH=CH)

Syntheses and Polymerizations of Dipropenylbenzenes

Synthesis of 1,2-Dipropenylbenzene 39

Phthalic dicarboxaldehyde (98%), ethyltriphenylphosphonium bromide (99%), and n-butyllithium (2.5 M solution in hexane) were purchased from Aldrich Chemical Company, Inc. Ethyltriphenylphosphonium bromide (85 g, 0.23 mole) was added to 500 mL of dry THF in an argon purged 3-neck flask. The mixture (suspension) was cooled to -50 °C, and 98.2 mL of 2.5 M n-butyllithium (0.24 mole) was slowly added to the mixture to form ylide. The reaction was conducted at -50 °C for 30 min changing from faint yellow to cherry red in color as the mixture was allowed to warm to room temperature. After 1 h at room temperature, the reaction mixture was cooled to -15 °C and a THF solution of 15 g (0.11 mole) of phthalic dicarboxaldehyde was added dropwise over a period of 60 min, then stirred at room temperature for 16 h. The reaction was quenched with aqueous $NaHCO_3$ (5g/L), and the mixture was extracted with ether. The ether layer was then dried and fractionally distilled to give pure product. It had the following yield and spectral properties:

Yield 38.7%

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (dd, 6 H, CH_3, *trans*), 1.88 (dd, 6 H, CH_3, *cis*), 5.80 (m, CH=), 6.13 (m, CH=), 7.10-7.50 (m, 4 H, phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3 (*cis*), 14.4 (*cis*), 18.7 (*trans*), 125.3, 126.1, 126.2, 126.7, 126.8, 127.2, 127.5, 128.9, 129.0, 129.2, 129.3, 129.5, 135.0, 135.7, 136.3, 136.5.

Elemental Analysis: Calculated for $C_{12}H_{14}$: C, 91.08; H, 8.92.
Found: C, 90.80, H, 8.99.

Synthesis of 1,3-Dipropenylbenzene 40

The 1,3-dipropenylbenzene was synthesized through a Wittig reaction of isophthaldehyde and ethyltriphenylphosphonium bromide. The same procedure for the synthesis of 1,2-dipropenylbenzene 39 was followed. The product 40 had the following yield and spectral properties:

Yield 35.6%

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.87 (m, 6 H, CH_3), 5.78 (m, *cis*, =CH-(CH3)), 6.22 (m, *trans*, =CH-(CH3)), 6.40 (br, 2 H, CH=(CH-CH_3)), 7.10-7.40 (br, 4 H, phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 14.7 (CH_3, *cis*) 18.5 (CH_3, *trans*), 123.6, 124.0, 124.3, 125.7, 126.5, 126.8, 127.0, 127.3, 128.0, 128.3, 128.6, 129.4, 130.0, 131.2, 137.5, 137.8, 138.1

Elemental Analysis: Calculated for $C_{12}H_{14}$: C, 91.08; H, 8.92
Found: C, 91.07, H, 8.91

Synthesis of Poly(1,2-phenylene vinylene) 41

The procedure for polymerization of 2,4-hexadiene was followed. The reaction was conducted at room temperature using 1.0 g (6.3 mmol) of 1,2-dipropenylbenzene 39 and 80 mg (0.094 mmol) of tungsten catalyst 1b. The product 41 was dissolved in chloroform, precipitated in methanol, and dried under a vacuum. It had the following yield and spectral properties:

Yield 64.7%

Molecular weight Integration of ^{1}H NMR Mn=870

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.84 (d, 6 H, CH_3), 6.10 (m, =CH-(CH_3)), 6.66-6.90 (D, CH=(CH-CH_3)), 7.08-7.85 (br, vinylene and phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.8 (CH_3), 126.2, 126.3, 126.5, 126.7, 126.8, 126.9, 127.0, 127.8, 127.9, 128.3, 128.6, 128.8, 129.0, 129.2, 129.7, 136.0, 136.2, 136.5, 136.8

UV (nm, $CHCl_3$) Broad 236-400, 2 maximum absorption: 278, 328.

Synthesis of Poly(1,3-phenylene vinylene) 42

The same procedure for the synthesis of poly(1,2-phenylene vinylene) was followed. The reaction was conducted at room temperature using 1.0 g (6.3 mmol) of 1,3-dipropenylbenzene 40 and 20 mg (0.023 mmol) of tungsten catalyst 1b. The product 42 had the following yield and spectral properties:

Yield 67.8%

Molecular weight Integration of ^{1}H NMR Mn=460

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.84 (d, 6 H, CH_3), 6.24-6.50 (m, 4 H, CH=CH-(CH_3)), 7.08-7.85 (br, vinylene and phenylene)

UV (nm, $CHCl_3$) Broad 236-360, 2 maximum absorption: 266, 306.

Synthesis and Polymerization of 8-Octenyl-*p*-propenylbenzene 44

Synthesis of 4-Bromo-1-propenylbenzene 43

In this reaction, the same procedure for synthesis of 1,2-dipropenylbenzene 40 was followed. The chemicals were purchased from Aldrich Chemical Company, Inc., and 37 g (0.20 mol) of 4-bromobenzaldehyde (99%), 78 g (0.21) of ethyltriphenyl phosphonium (99%), 88 mL of 2.5 M solution of butyllithium were used in the reaction. The compound 43 had the following yield and spectral properties:

Yield 32.6%

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.85 (d, 3 H, CH_3), 5.82 and 6.10-6.41 (m, 2 H, *cis* and *trans* -CH=CH-), 7.26 (dd, 2 H, phenylene), 7.42 (dd, 2 H, phenylene).

Synthesis of 8-Octenyl-*p*-propenylbenzene 44

In an argon-filled dry box and at 0 °C, 8-octenyl magnesium bromide was added dropwise into a solution of 12 g (63 mmol) of 4-bromo-1-propenylbenzene 43 and 0.17 g (0.32 mmol) of [1,3-bis(diphenylphosphino)propane]nickel (II) chloride (Ni[dppp]Cl_2,

Aldrich) in anhydrous ether. The mixture was stirred at room temperature for 1 h and then refluxed for 20 h. After cooling down to room temperature, the resulting mixture was hydrolyzed with 1 M HCl aqueous solution and extracted by ether twice. The organic portion was collected, and the ether was then removed under reduced pressure. The fractional distillation of the mixture gave a pure product of 4.54 g. It had the following yield and spectral properties:

Yield 31.4%

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20-1.51 (br, 6 H, CH_2), 1.51-78 (br, 2 H, CH_2), 1.88 (d, 3 H, CH_3), 2.04 (q, 2 H, CH_2), 2.58 (m, 2 H, CH_2), 4.94 (m, 2 H, $=CH_2$), 5.78 and 6.08-6.50 (m, 3 H, -CH=), 7.3-7.48 (m, 4 H, phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 14.7 (CH_3,*cis*), 18.45 (CH_3,*trans*), 28.9, 29.0, 29.1, 29.2, 31.4, 33.8, 35.6, 35.7, 114.2, 124.6, 125.7, 126.0, 128.1, 128.5, 128.7, 129.8, 130.9, 135.0, 135.4, 139.1, 141.1, 141.4

Elemental Analysis: Calculated for $C_{17}H_{24}$: C, 89.41; H, 10.59
Found: C, 89.26; H, 10.67

Polymerization of 8-Octenyl-*p*-propenylbenzene 44

Poly(hexamethylene *p*-phenylene vinylene) 45 was obtained through the ADMET polymerization of 8-octenyl-p-propenylbenzene 44. The same procedure for the polymerization of 1,2-dipropenylbenzene was followed. The reaction was conducted at room temperature using 1.0 g (4.4 mmol) of 8-octenyl-p-propenylbenzene 44 and 20 mg (0.023 mmol) of tungsten catalyst 1b. The product 45 had the following yield and spectral properties:

Yield 72.5%

Molecular weight Integration of ^1H NMR Mn=1890

^1H NMR (200 MHz, $CDCl_3$) δ 1.21-1.45 (br, CH_2), 1.45-1.65 (br, CH_2), 1.83 (d, 6 H, CH3), 1.85-2.3 (br, CH_2), 2.18 (q, CH_2), 2.56 (t, CH_2), 5.36 (m, CH=CH), 6.18 (m, CH=CH), 6.32 (m, CH=CH), 7.03-7.46 (m, phenylene and vinylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.4 (CH_3), 27.2, 28.8, 29.0, 29.1, 29.4, 29.5, 31.4, 32.6, 33.0, 35.6, 124.6, 125.6, 125.8, 126.1, 126.3, 127.7, 128.5, 128.7, 129.6, 129.7, 130.0, 130.1, 130.3, 130.9, 135.4, 141.5

Syntheses of Poly(phenylenevinylene-co-octenamers)

Synthesis of Poly(1,2-phenylenevinylene-co-octenamer) 1:1 Ratio 46

In an argon-filled dry box, 0.316 g (2.00 mmol) of 1,3-dipropenylbenzene, 0.276 g (2.00 mmol) of 1,9-decadiene and 20 mg (0.026 mmol) of molybdenum catalyst 1c were mixed in a 30 mL round bottom reaction flask. Polymerization was carried on at 30 °C with stirring, and small molecules generated in the reaction were removed by intermittent application of vacuum. After the reaction mixture was solidified, the chloroform was added to dissolve the mixture. The copolymer 46 was then precipitated in methanol and dried under a vacuum. It had the following yield and spectral properties:

Yield 65.7%

Molecular weight GPC Mn=1090, Mw=1440, Mw/Mn=1.31

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.20-1.55 (br, CH_2), 1.63 (d, CH_3) 1.76 (d, CH_3), 1.88-2.27, (m, CH_2), 5.38 (m, nonconj., CH=CH) 5.48-5.82, (m, conj. CH=CH), 5.93-6.45, (m, conj. CH=CH)

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.1, 27.4, 29.2, 29.5, 29.6, 29.8, 32.8, 33.0, 33.1, 124.7, 130.1, 130.6, 130.8, 131.0, 131.9, 132.6, 132.7, 133.2, 134.7, 135.3, 135.4

UV (CHCl3, nm) Broad 236-350

Synthesis of Poly(1,2-phenylenevinylene-co-octenamer) 4:1 Ratio 47

In this synthesis, the same procedure for the 1:1 ratio copolymerization was followed. The mole ratio of 1,2-dipropenylbenzene (0.632 g) to 1,9-decadiene (0.138 g) was 4:1. The copolymer 47 had the following yield and spectral properties:

Yield 63.4%

Molecular weight GPC Mn=670, Mw=830, Mw/Mn=1.25

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.20-1.65 (br, CH_2), 1.90(d, CH_2), 2.23 (d, CH_2), 6.10, (m, conj. CH=CH), 6.70, (m, conj. CH=CH), 7.10-7.80 (phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.8, 29.1, 29.6, 33.3, 33.4, 126.3, 126.4, 127.0, 127.2, 127.6, 127.7, 128.8, 128.9, 129.0, 129.5, 129.7, 133.1, 133.0, 134.2, 135.4, 135.8, 136.4, 136.8, 136.9

UV ($CHCl_3$, nm) Broad 236-370

Synthesis of Poly(1,2-phenylenevinylene-co-octenamer) 1:4 Ratio 48

In this synthesis, the same procedure for the 1:1 ratio copolymerization was followed. The mole ratio of 1,2-dipropenylbenzene (0.158 g) to 1,9-decadiene (0.552 g) was 1:4. The copolymer 48 had the following yield and spectral properties:

Yield 66.3%

Molecular weight GPC Mn=2110, Mw=4040, Mw/Mn=1.97

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.20-1.65 (br, CH_2), 1.65 (s, CH_2) 1.85-2.10 (br, CH_2), 2,20 (s, CH_2), 5.38 (s, nonconj., CH=CH), 6.15-6.45, (m, conj. CH=CH), 7.15-7.35 (phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 27.2, 29.0, 29.6, 29.7, 32.6, 33.0, 123.6,124.4, 127.5, 128.6, 129.7, 129.9, 130.3, 131.2, 138.1

UV (CHCl3, nm) Broad 236-290

Synthesis of Poly(octenamer-co-1,2-phenylenevinylene) 49

In an argon-filled dry box, 0.276 g (2.00 mmol) of 1,9-decadiene and 15 mg (0.020 mmol) of molybdenum catalyst 1c were mixed in a 30 mL round bottom reaction flask. The reaction flask was then sealed and moved to a vacuum line. Polymerization was carried on at room temperature. After solid polyoctenamer was formed, 0.316 g (2.0 mmol) of 1,2-dipropenylbenzene was added to the polyoctenamer, and polymerization was continued for 12 hours

at room temperature. The copolymer was dissolved in chloroform, precipitated from methanol, and dried under a vacuum. It had the following yield and spectral properties:

Yield 59.7%

Molecular weight GPC Mn=1780, Mw=4080, Mw/Mn=2.29

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.20-1.60 (br, CH_2), 1.65 (d, CH_2) 1.88 (d, CH_3), 2.23 (d, CH_2), 5.38 (s, nonconj., CH=CH), 6.15-6.45, (m, conj. CH=CH), 7.10 (s, vinylene), 7.13-7.60 (m, phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.5, 27.2, 28.7, 29.0, 29.2, 29.3, 29.5, 29.6, 29.7, 32.6, 33.0, 123.5, 123.6, 124.2, 124.4, 124.6, 124.9, 125.0, 125.2, 125.6, 128.7, 129.6, 129.7, 130.3, 130.4, 131.0, 131.1, 131.5, 137.5, 138.1, 138.3

UV (CHCl3, nm) Broad 236-350.

Synthesis of Block Poly(1,2-phenylenevinylene-co-octenamer) 50

In an argon-filled dry box, 0.32 g (2.0 mmol) of 1,2-dipropenylbenzene and 15 mg (0.020 mmol) of molybdenum catalyst 1c were mixed in a 30 mL round bottom reaction flask. The reaction flask was then sealed and moved to a vacuum line. Polymerization was carried out at room temperature with stirring. After poly(1,2-phenylenevinylene) was formed, 0.276 g (2.0 mmol) of 1,9-decadiene was then added into the poly(1,2-phenylene vinylene), and polymerization was continued for 12 h at room temperature. The copolymer 50 was dissolved in chloroform, precipitated from methanol, and dried under a vacuum. It had the following yield and spectral properties:

Yield 63.6%

Molecular weight GPC Mn=1400, Mw=2300, Mw/Mn=1.65

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.20-1.60 (br, CH_2), 1.65 (s, CH_2), 1.95 (s CH_2), 2.20 (s, CH_2), 5.38 (s, nonconj., CH=CH), 6.00-6.20, (br, conj. CH=CH), 6.70, (d, conj. CH=CH), 7.10-7.65 (vinylene and phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 27.2, 29.0, 29.3, 29.4, 29.5, 29.6, 29.7, 32.6, 33.3, 33.4, 126.2, 126.3, 126.7, 126.9, 127.2, 127.6, 127.7, 127.8, 128.1, 128.3, 128.5, 128.7, 129.0, 129.5, 129.7, 130.3, 134.0, 134.1, 134.2, 135.5, 136.7

UV (CHCl3, nm) Broad 236-390

Synthesis of Poly(1,3-phenylenevinylene-co-octenamer) 1:1 Ratio 51

In this synthesis, the same procedure for the synthesis of poly(1,2-phenylenevinylene-co-octenamer) 46 was followed. The mole ratio of 1,3-dipropenylbenzene (0.316 g) to 1,9-decadiene (0.276 g) was 1:1. The copolymer 51 had the following yield and spectral properties:

Yield 66.7%

Molecular weight GPC Mn=1240, Mw=1720, Mw/Mn=1.39

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.20-1.60 (br, CH_2), 1.65 (d, CH_2), 1.85-2.10 (br, CH_2) 2.23 (d, CH_2), 5.38 (s, nonconj., CH=CH), 6.05, (m, conj. CH=CH), 6.65, (m, conj. CH=CH), 7.10-7.70 (phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 27.2, 28.5, 28.7, 28.8, 29.0, 29.1, 29.4, 29.6, 29.8, 32.6, 33.1, 33.3, 125.3, 125.8, 126.0, 126.3, 126.7, 126.8, 127.0, 127.2, 127.6, 127.8, 128.3, 128.4, 128.8, 128.9, 129.0, 129.4, 129.5, 129.7, 129.9, 130.3, 130.4, 132.4, 133.1, 133.2, 133.3, 134.0, 134.2, 135.5, 135.8, 136.8

UV (CHCl3, nm) Broad 236-350.

Synthesis of Poly(1,3-phenylenevinylene-co-octenamer) 4:1 Ratio 52

In this synthesis, the same procedure for the synthesis of poly(1,2-phenylenevinylene-co-octenamer) 46 was followed. The mole ratio of 1,3-dipropenylbenzene (0.632 g) to 1,9-decadiene (0.138 g) was 4:1. The copolymer 52 had the following yield and spectral properties:

Yield 64.3%

Molecular weight GPC Mn=610, Mw=790, Mw/Mn=1.30

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.30-1.65 (br, CH_2), 1.85-2.00 (br, CH_2) 2.23 (t, CH_2), 6.15-6.50 (m, conj. CH=CH), 7.10 (s, vinylene), 7.12-7.60 (phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.5, 29.1, 29.3, 33.0, 123.6, 124.1, 124.3, 124.8, 124.9, 125.1, 125.2, 125.3, 125.7, 125.8, 126.1, 128.5, 128.6, 128.7, 129.0, 129.6, 129.8, 130.9, 131.0, 131.2, 131.5, 137.4, 137.5, 137.7, 138.0, 138.3

UV (CHCl3, nm) Broad 236-350

Synthesis of Poly(1,3-phenylenevinylene-co-octenamer) 1:4 Ratio 53

In this synthesis, the same procedure for the synthesis of poly(1,2-phenylenevinylene-co-octenamer) 46 was followed. The mole ratio of 1,3-dipropenylbenzene (0.158 g) to 1,9-decadiene (0.552 g) was 1:4. The copolymer 53 had the following yield and spectral properties:

Yield 67.6%

Molecular weight GPC Mn=2640, Mw=5790, Mw/Mn=2.20

^{1}H NMR (200 MHz, $CDCl_3$), δ 1.20-1.60 (br, CH_2), 1.65 (d, CH_2), 1.85-2.10 (br, CH_2), 2.20 (m, CH_2), 5.38 (s, nonconj., CH=CH), 6.10-6.45, (m, conj. CH=CH), 7.15-7.40 (phenylene)

^{13}C NMR (50 MHz, $CDCl_3$) δ 27.2, 29.0, 29.4, 29.6, 32.6, 33.0, 123.6, 124.4, 128.6, 129.7, 129.8, 130.3, 131.1, 131.2, 138.1

UV (CHCl3, nm) Broad 236-290

Metathesis Reaction of Propenylbenzene and 1-Nonene

In an argon-filled dry box, a mixture of propenylbenzene 54 and 1-nonene 55 were mixed in a 4 mL vial. The total weight of the mixture was 0.5 g, and the mole ratios of compound 54 to 55 were 100:0, 90:1, 75:25, 50:50, 25:75, 10:90, and 0:100, respectively. The mixture was then added to a 30 mL round bottom reaction flask, which contained 10 mg (0.026 mmol) of molybdenum catalyst 1c.

The reaction was carried out at room temperature with stirring, and the ethylene, propene, and butene generated in the reaction was removed by intermittent application of a vacuum. After the reaction was completed, the mixture of products was characterized by ^1H NMR spectroscopy. The products, stilbene 56, 1-phenyl-1-nonene 57, and 8-hexadecene 58, had the following ^1H NMR resonances.

^1H NMR (200 MHz, $CDCl_3$)

Stilbene	δ	7.10 (s CH=CH), 7.12-7.55 (m, phenyl)
1-Phenyl-1-nonene	δ	0.9 (t, CH_3), 1.15-1.6 (br, CH_2), 2.20 (m, CH_2), 6.13-6.46 (m, CH=CH), 7.12-7.40 (m, phenyl)
8-Hexadecene	δ	0.9 (t, CH_3), 1.15-1.6 (br, CH_2), 1.97 (m, CH_2), 5.38 (m, CH=CH)

CHAPTER 3

REACTIVITIES OF CONJUGATED DIENES AND TRIENES IN ADMET POLYMERIZATION

Since acyclic diene metathesis (ADMET) chemistry was first established as a new equilibrium, step, condensation polymerization in 1988, many high molecular weight unsaturated polymers and copolymers[149-159] have been synthesized through ADMET polymerization. Prior to this dissertation, the monomers used in ADMET polymerization have possessed a spacer group between the two olefins (R in Figure 3.1).

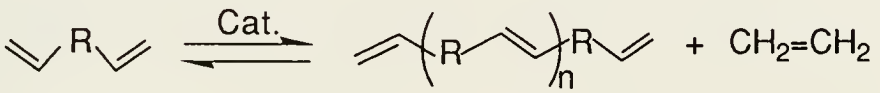


Figure 3.1. Acyclic diene metathesis (ADMET) polymerization.

This research studies the reactivities of conjugated dienes (no spacer group) and trienes in ADMET polymerization using Schrock's well-defined metal alkylidene catalysts. A monomer having two olefins directly conjugated together has not been studied in previous ADMET research. In broadening the scope of ADMET polymerization, it is meaningful to examine the chemistry of conjugated dienes in this polymerization.

Internal conjugated monomers (a CH_3 group at each end), 2,4-hexadiene and 2,4,6-octatriene, and terminal conjugated monomers (two hydrogen atoms at each end), 1,3-butadiene and 1,3,5-hexatriene were used. The different reactivities between internal conjugated monomers and terminal conjugated monomers were investigated. The copolymerization of 2,4-hexadiene and nonconjugated dienes was also examined.

The Polymerization Chemistry of Internal Conjugated Dienes

An internal conjugated diene, 2,4-hexadiene 2, was the first monomer for examining the polymerizability of conjugated dienes. The 2,4-hexadiene was selected because it was a commercially available liquid, and it was easy to purify in comparison to gaseous 1,3-butadiene. The ADMET polymerization of 2,4-hexadiene was rapid, and the polymer obtained was a conjugated methyl-terminated polyacetylene (Figure 3.2).

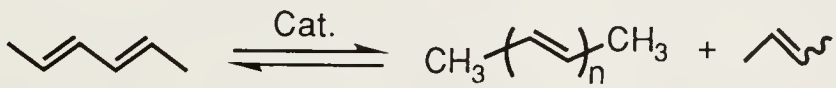


Figure 3.2. ADMET polymerization of 2,4-hexadiene.

According to the general ADMET polymerization mechanism, the reaction cycle of the polymerization of 2,4-hexadiene could be described as in Figure 3.3. One double bond of 2,4-hexadiene reacted

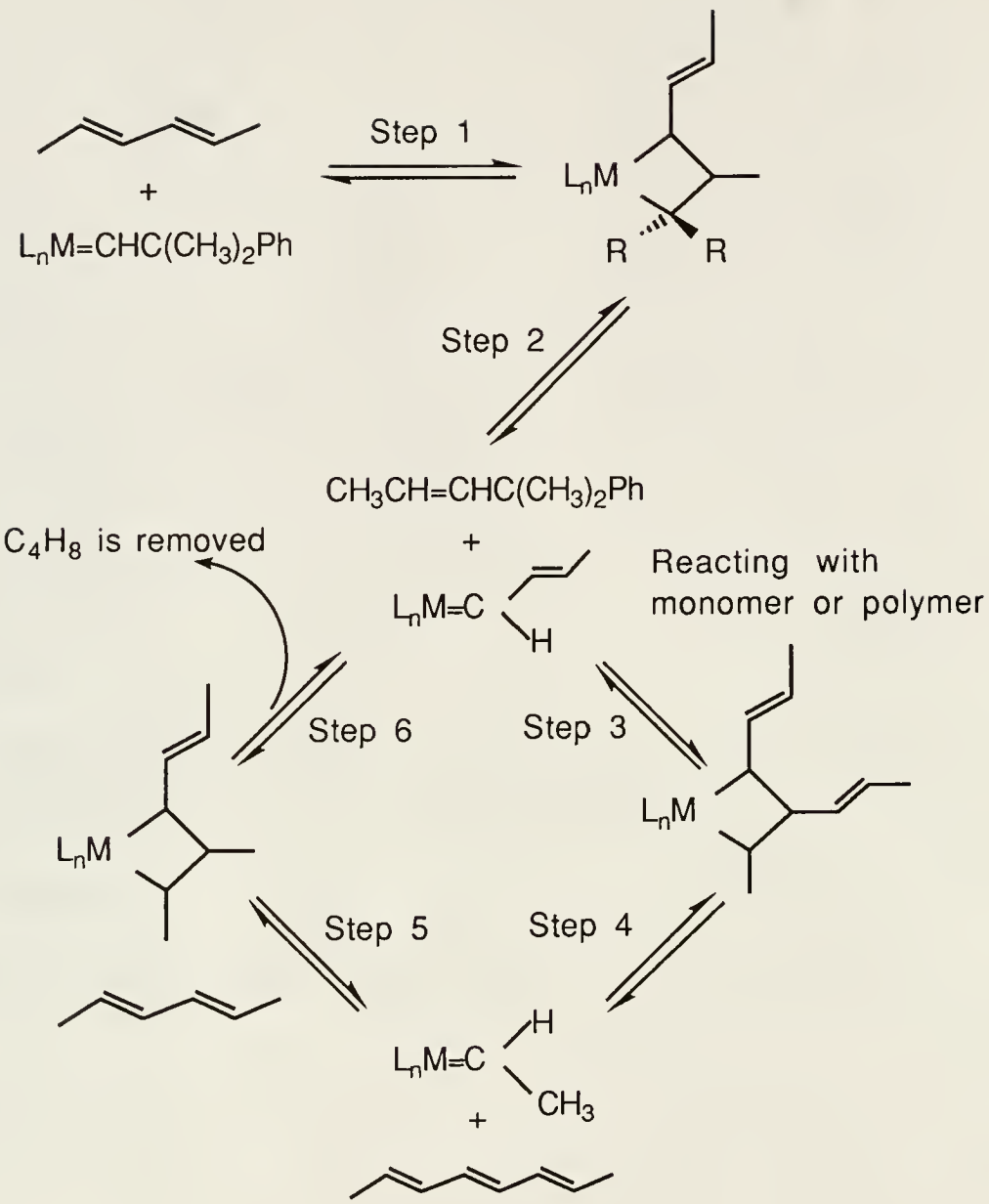


Figure 3.3. The ADMET polymerization cycle for 2,4-hexadiene.

with the initial metal alkylidene to form a metallacyclobutane (Figure 3, Step 1), which then was rearranged to form a second alkylidene and a neophyl alkene (Step 2). This alkylidene then reacted with the olefin moiety of another monomer to form a second metallacyclobutane which then was rearranged to dimer and a third metal alkylidene (Steps 3 and 4). The reaction process was continued as a cycle (Steps 3-6) to obtain longer chain molecules and to release 2-butene.

In this ADMET polymerization, the product, 2-butene, was collected as a 4:1 mixture of the *trans* and *cis* isomers, respectively, as determined by NMR spectroscopy (Figure 3.4). The generation of 2-butene was an evidence to demonstrate that this polymerization was a metathesis condensation reaction.

The polyacetylene product, 3a, was a low molecular weight oligomer and was characterized by NMR spectroscopy using chloroform-*d* as solvent. The NMR spectra of these polyacetylene oligomers (Figure 3.5) clearly showed that methyl groups were present at both ends of the polyacetylene chain. The protons of the terminal methyl groups were at 1.8 ppm, and the protons of the conjugated double bonds were found mainly between 6.0-6.4 ppm. The peak near 5.7 ppm was assigned to the protons of the conjugated double bonds at the ends of the polyacetylene chain. Solid state ^{13}C NMR spectroscopy also confirmed the existence of this polyacetylene's structure.

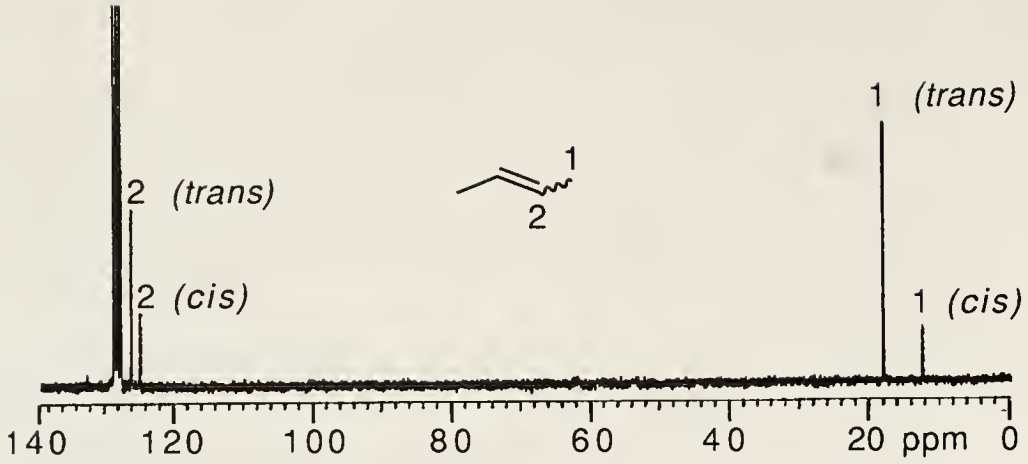


Figure 3.4. ^{13}C NMR spectrum of 2-butene collected in ADMET polymerization of 2,4-hexadiene.

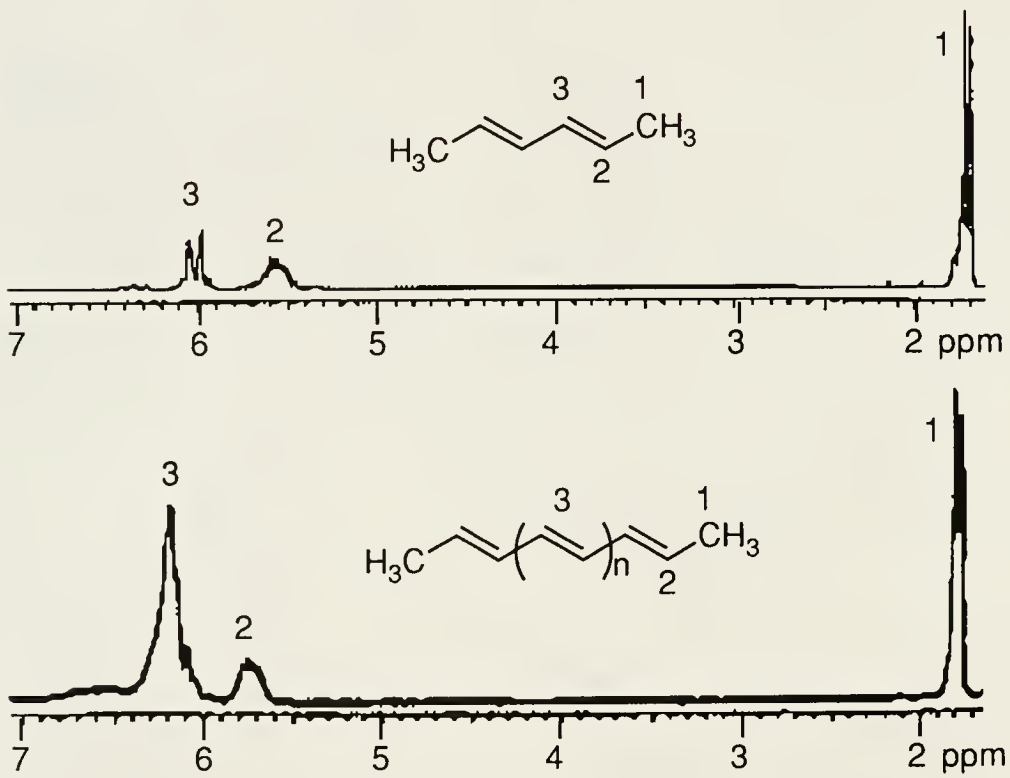


Figure 3.5. ^{1}H NMR spectra of 2,4-hexadiene and its bulk polymerization product, methyl-terminated polyacetylene.

According to the ^1H NMR integration values, polyacetylene oligomers from the bulk polymerization of 2,4-hexadiene were an average of 6-10 repeat units. Since higher molecular weight polyacetylene is partially soluble in $CDCl_3$, the actual average molecular weight of the entire sample could be higher than that calculated from the NMR spectra. Mass spectrometry (MS) showed that the highest detectable length is 20 repeat units, and gel permeation chromatography (GPC) vs. polybutadiene standards shows an average of 15 repeat units. Only polyacetylene oligomers were produced in this step, condensation, equilibrium polymerization because the methyl terminated polyacetylenes have high melting points[18] (4-ene, mp 115 °C; 5-ene, mp 150 °C) and solidify at low degrees of polymerization. In this manner, the terminal olefins of the polyacetylene oligomers are restricted from further metathesis condensation.

The UV spectra of 2,4-hexadiene and the soluble portion of its polymers are shown in Figure 3.6. According to the work of Nayler[162] and Spangler,[163] an unsubstituted methyl-terminated polyacetylene oligomer containing more than three double bonds showed three main absorbances. Compared with the UV spectra of individual methyl terminated polyacetylene oligomers (3-ene to 12-ene units) in Nayler's paper, the multiple UV absorption of the polyacetylenes here could be attributed to the different polyacetylene chain lengths. The highest absorption of the methyl-terminated polyacetylene from bulk polymerization was at 423 nm, which could be from the polyacetylene containing 8 conjugated repeat units. The middle length polyacetylene had an absorption at

349 nm, which could be assigned to the 5 repeat units. The chain length exhibited by this UV spectrum was consistent with that from the NMR spectrum for the same sample.

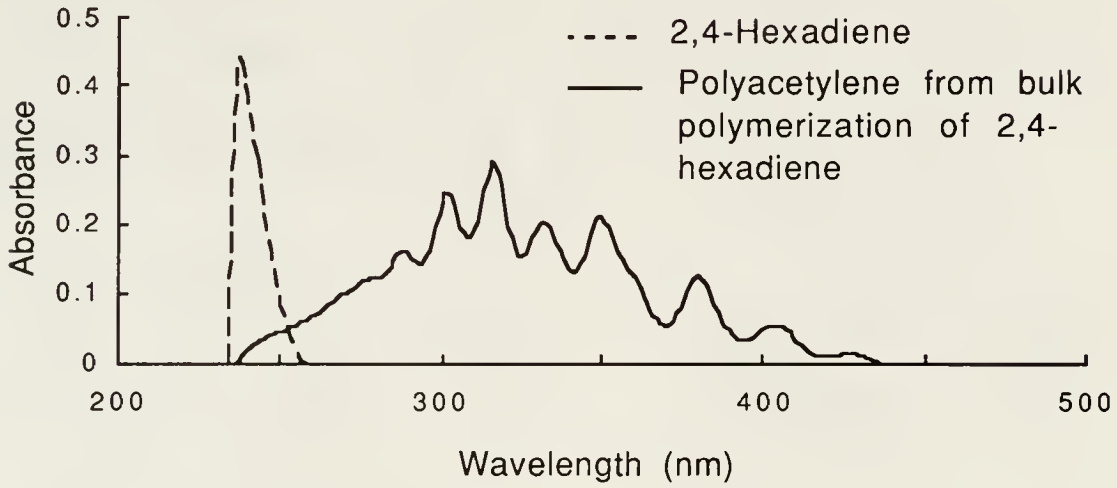


Figure 3.6. The UV spectra of 2,4-hexadiene and its bulk polymerization polyacetylene.

Solution ADMET Polymerization *versus* Bulk ADMET Polymerization

There are two techniques in ADMET polymerization to increase the molecular weight of a polymer product. One technique is to raise the reaction temperature, where the viscosity of the polymer decreases with an increase of temperature. The molecular weight, therefore, increases with continuing condensation of terminal olefin and removal of small molecules from the reaction system. This method was limited in ADMET polymerization by the deactivation of Schrock's catalyst at temperature higher than 65 °C.

A second technique to increase the molecular weight of a polymer is to use a solution polymerization method, where the molecular weight of the polymer increases until the high molecular weight polymers precipitate from solution or the molecular weight of the polymer reaches a point where the terminal olefin metathesis condensation is stopped.

In the ADMET polymerization of 2,4-hexadiene, the low molecular weight polyacetylene oligomers were soluble in toluene solution, which allowed the polyacetylene molecular weight to increase by solution polymerization. When 2,4-hexadiene was dissolved in toluene, followed by the addition of a catalyst, the polyacetylene oligomers remained soluble for approximately 10 min before precipitating. In this manner, polyacetylenes with an average of 10-15 double bond units were prepared as determined by NMR spectroscopy. Mass spectrometry (MS) showed that the highest detectable length for the solution polymerization polyacetylenes from 2,4-hexadiene is 21 repeat units, and gel permeation chromatography (GPC) versus polybutadiene standards showed an average of 20 repeat units. The solution (1.0 M) polymerization product showed a higher molecular weight than did the bulk polymerization product.

The UV spectra (Figure 3.7) confirmed that solution polymerization polyacetylenes had longer lengths than did bulk polymerization polyacetylenes. A slightly longer wavelength absorption for the solution polymerization polyacetylenes was observed in Figure 3.7. The highest absorption wavelength at 470 nm represented a polyacetylene length higher than 10 repeat units.

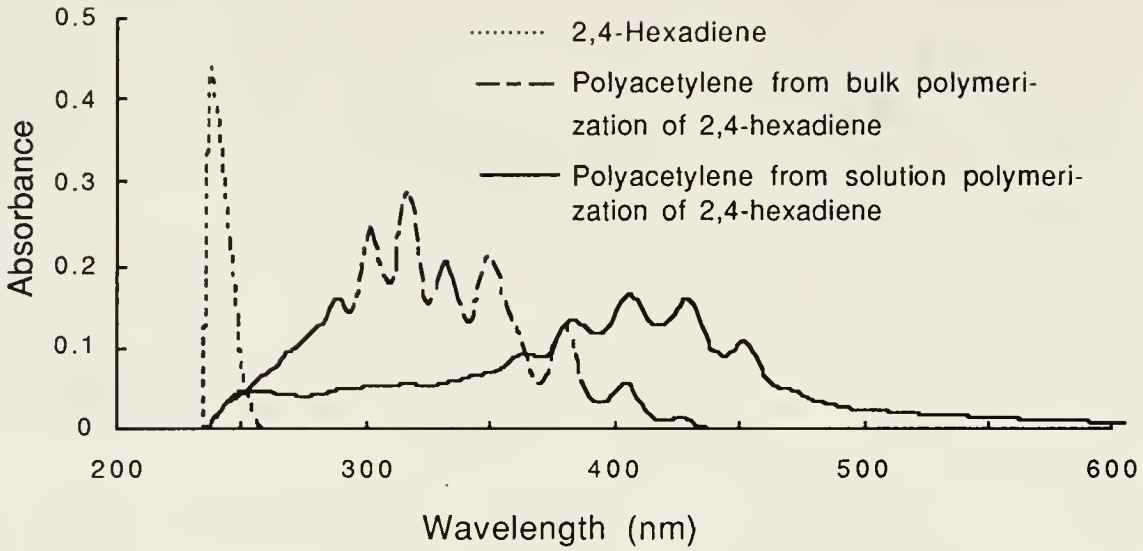


Figure 3.7. UV spectra of 2,4-hexadiene and its bulk and solution ADMET polyacetylenes.

ADMET Polymerization of an Internal Conjugated Triene, 2,4,6-Octatriene

Bulk polymerization of 2,4,6-octatriene was conducted at room temperature using the Lewis acid-free molybdenum catalyst 1c (Figure 3.8). Methyl-terminated polyacetylene oligomers were obtained.

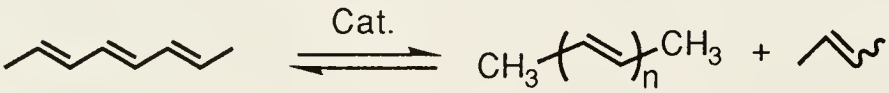


Figure 3.8. ADMET polymerization of 2,4,6-octatriene.

Polyacetylene oligomers obtained through bulk polymerization of 2,4,6-octatriene had molecular lengths and physical properties similar to those of 2,4-hexadiene. According to ^1H NMR integration values, methyl-terminated polyacetylenes from the bulk polymerization of 2,4,6-octatriene were an average of 10 repeat units. Gel permeation chromatography (GPC) versus polybutadiene standards gave a number average molecular weight of 357 (DP 12), weight average molecular weight of 668, and a molecular weight distribution of 1.72.

The UV spectrum of the polyacetylenes generated from the bulk polymerization of 2,4,6-octatriene (Figure 3.9) was similar to that of the polyacetylenes obtained from 2,4-hexadiene, except for the different distributions of the two samples, which showed a slightly higher average molecular weight for the polyacetylene from 2,4,6-octatriene than that from 2,4-hexadiene.

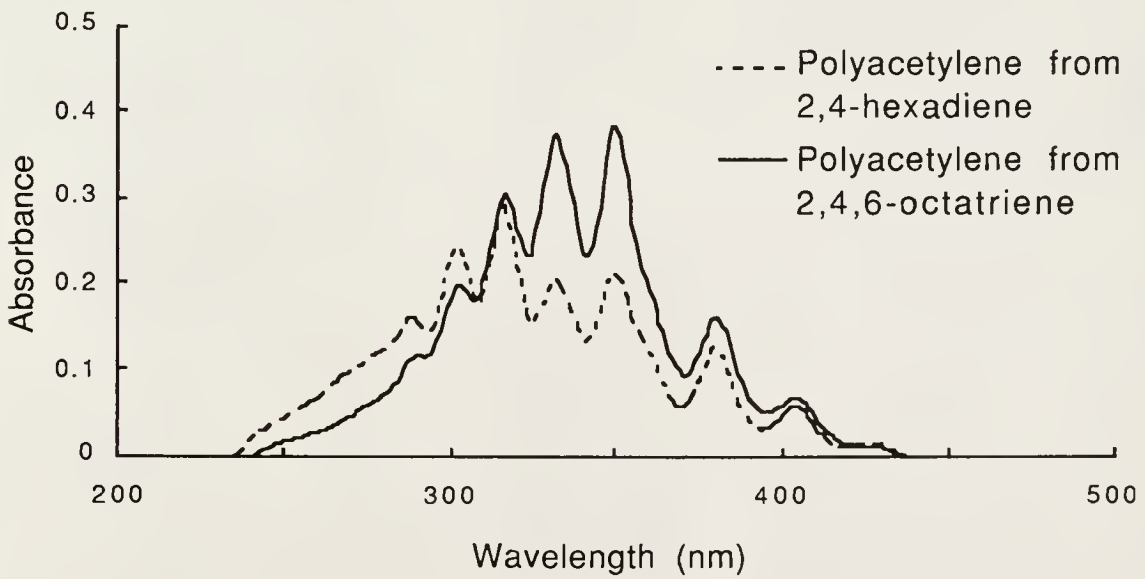


Figure 3.9. UV spectra of polyacetylenes from ADMET polymerization of 2,4-hexadiene and 2,4,6-octatriene.

The ^{13}C NMR resonances of *tert*-butyl-capped polyacetylene oligomers had been reported by Schrock *et al.*[129] The major resonances of all *trans* isomers were at 131-134 ppm and alternating *trans-cis* isomers were at 127-130 ppm (Table 3.1), which was consistent with the resonances of cis polyacetylene at 126-129 ppm[48]. Compared with these reported data, the carbon resonances of polyacetylene oligomers from bulk polymerization of 2,4,6-octatriene were mainly at 131.9-133.4 ppm (Table 3.2), which showed the dominated configurations of the polymer to be *trans* isomers.

Table 3.1. ^{13}C NMR resonance of *tert*-butyl-capped polyacetylene oligomers.[131]

Isomer[a]	1	2	3	4	5	6	7	8	9
$7t_7$	146.7	125.5	133.9	131.1	132.4	132.9	133.3		
$9t_9$	146.9	125.6	134.1	131.1	132.4	132.9	133.2	133.5	133.6
$7t(ct)_3$	147.9	120.6	131.1	127.6	128.2	129.2	129.8		
$9t(ct)_4$	148.0	120.6	131.3	127.6	128.2	129.1	129.8	130.4	129.5

[a]The $7t_7$ refers to 7 double bonds with all *trans* structure; $7t(ct)_4$ refers to 7 double bonds with alternated *trans-cis* structure; $9t_9$ and $9t(ct)_4$ are as same as above.

Table 3.2. ^{13}C NMR resonance of polyacetylene oligomers from 2,4,6-octatriene.

ppm	128.0	129.4	129.8	130.6	130.7	131.9	132.0	132.3	132.4
Intensity	43.0	61.0	37.1	82.2	61.3	78.5	68.8	79.4	56.6
ppm	132.7	132.8	132.9	133.0	133.2	133.2	133.3	133.4	
Intensity	24.0	44.1	21.2	37.7	30.9	30.7	32.7	32.0	

An Investigation of the Reactions of Terminal Conjugated Dienes and Trienes with a Molybdenum Catalyst

In the terminology of this dissertation, the simplest terminal conjugated diene is 1,3-butadiene, and the simplest internal conjugated diene is 2,4-hexadiene. The difference between 1,3-butadiene and 2,4-hexadiene is that the former has two hydrogen atoms at each end carbon, whereas the latter has one CH_3 group and one H atom at each end carbon.

The potential monomer 1,3-butadiene was carefully purified with a sodium mirror to exclude possible moisture and oxygen, and the attempted polymerization reaction was then conducted in a sealed flask at room temperature. Unlike the polymerization of 2,4-hexadiene, where the reaction was fast and solid oligomers were formed in less than 5 min, 1,3-butadiene did not produce any observed ADMET polymer after 24 h of stirring at room temperature. Only unreacted monomer remained in the reaction system.

Regarding why polymerization of 1,3-butadiene did not occur, ^1H NMR spectroscopy was used to examine the reaction mixture of 1,3-butadiene and the molybdenum catalyst 1c. The ^1H NMR spectrum (Figure 3.10) showed that a metathesis exchange reaction (Figure 3.11) had occurred, since the resonances at 5.0 ppm and 6.0 ppm for sp^2 protons of 3-methyl-3-phenyl-1-butene were observed (see Figure 3.10).

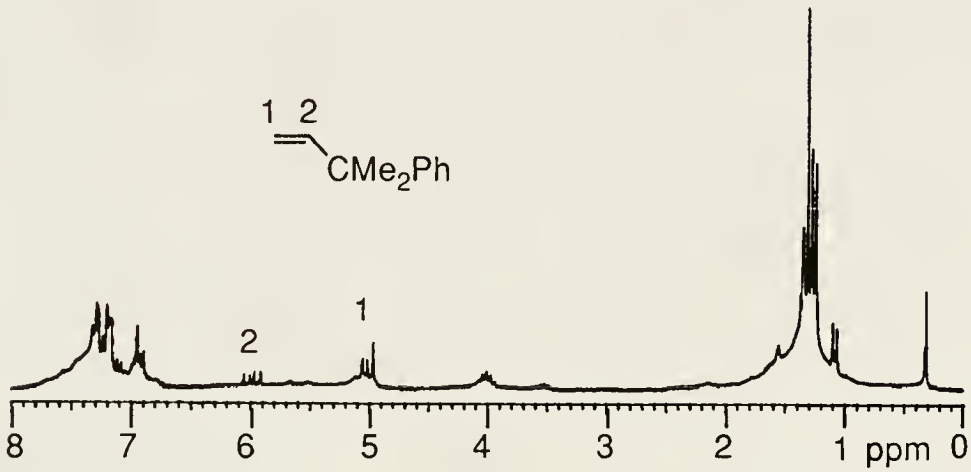


Figure 3.10 ^1H NMR spectrum (C_6D_6) of the reaction product after 4 h between 1,3-butadiene and molybdenum catalyst 1c.

If ADMET polymerization of 1,3-butadiene had occurred, the newly formed vinyl alkylidene (see Figure 3.11) should have reacted with a second 1,3-butadiene to form 1,3,5-hexatriene and a molecule of ethylene. This did not occur. Instead, the molybdenum catalyst apparently decomposed and catalyzed a reaction yielding a small amount of crosslinking polymer. The mechanism of the decomposition of molybdenum catalyst by 1,3-butadiene is not clear.

The conjugated terminal triene, 1,3,5-hexatriene, exhibited the same behavior with molybdenum catalyst 1c as did 1,3-

butadiene. A small amount of crosslinked polymer was formed when 1,3,5-hexatriene and molybdenum catalyst were mixed and stirred at room temperature for 24 h. The molybdenum catalyst decomposed faster in 1,3,5-hexatriene than in 1,3-butadiene.

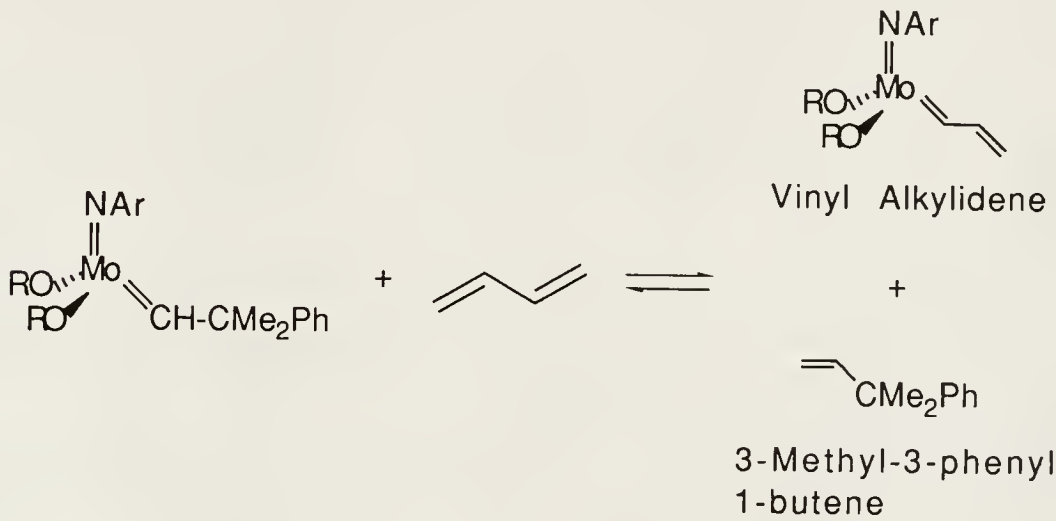


Figure 3.11. A metathesis exchange reaction between 1,3-butadiene and molybdenum catalyst.

Copolymerization of 2,4-Hexadiene and a Nonconjugated Diene

Copolymerization allows the synthesis of a large number of products by variations in the nature and amount of the two monomer units in the copolymer product. From a technological viewpoint, copolymerization greatly increases the ability of the polymer scientist to tailor-make a polymer product with specific desired properties. Much of our knowledge of the reactivities of monomers arises from copolymerization studies. The behavior of monomers in

copolymerization reaction is especially useful for studying the effect of chemical structure on reactivity.

Copolymers are generally divided into the four following categories according to their structure: random (Figure 3.12, (a)), alternating (Figure 3.12, (b)), block (Figure 3.12, (c)), and graft (Figure 3.12, (d)).

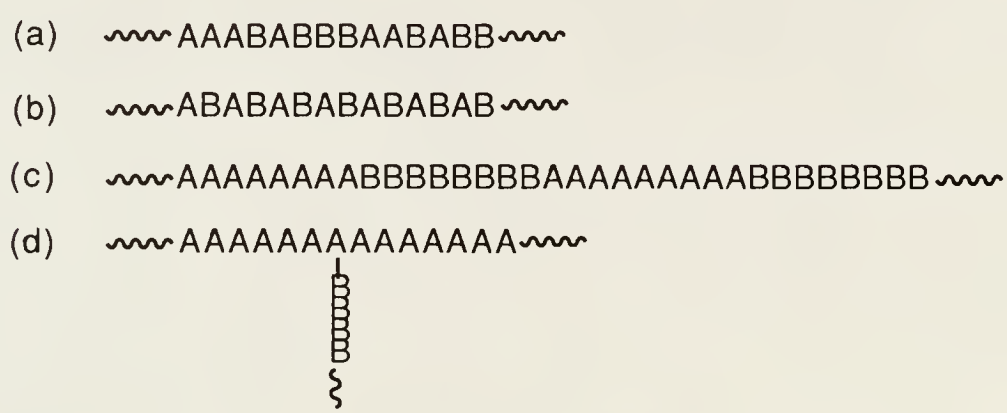
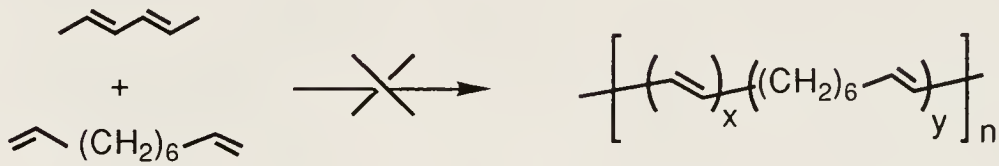


Figure 3.12. The four different categories of copolymers

In this section, copolymerization of a conjugated diene and a nonconjugated diene was aimed at producing poly(acetylene-co-octenamer), a combination of polyacetylene and polyoctenamer, which might have useful properties. The copolymerization was also aimed at examining the relative reactivities of two monomers in the ADMET copolymerization reaction.

The first reaction attempted was to copolymerize a conjugate terminal diene, 2,4-hexadiene, and a nonconjugated terminal diene, 1,9-decadiene (Figure 3.13). This copolymerization was not successful using either tungsten or molybdenum catalysts. In both cases the ADMET reaction started but gradually stopped after 30

min. Only unreacted monomers and polyoctenamer oligomers were found in the reaction mixture.



Poly(acetylene-co-octenamer)

Figure 3.13. Attempt to copolymerize 2,4-hexadiene and 1,9-decadiene.

Apparently, 1,3-butadiene is formed through a metathesis exchange reaction between 2,4-hexadiene and 1,9-decadiene (Figure 3.14), and subsequently the catalyst is decomposed by the newly formed 1,3-butadiene.

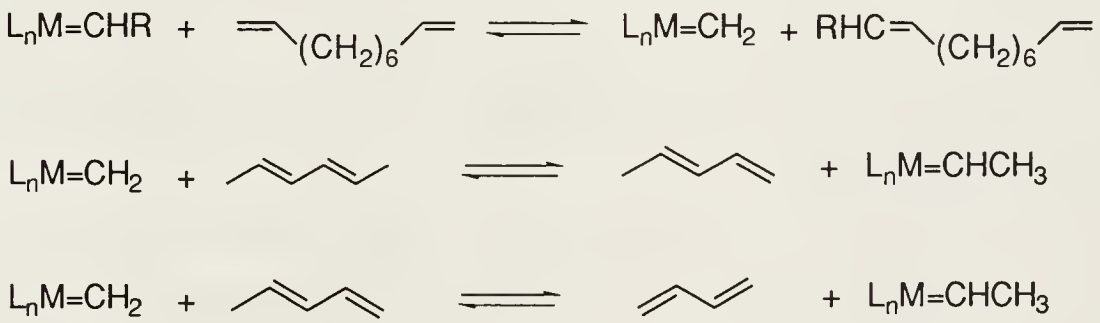
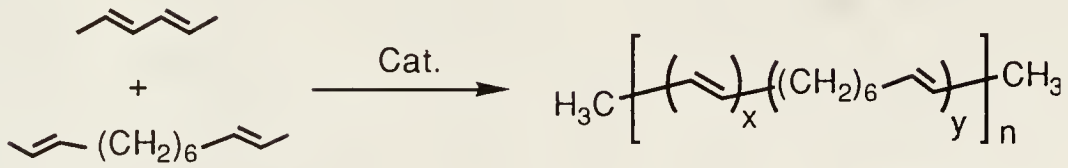


Figure 3.14. Formation of 1,3-butadiene through metathesis exchange reaction.

Poly(acetylene-co-octenamer) copolymers were successfully synthesized through copolymerization of 2,4-hexadiene and an nonconjugated internal diene, 2,10-dodecadiene, using the molybdenum catalyst (Figure 3.15). Different monomer ratios were applied in copolymerization to control copolymer structures and to

investigate the reactivities of conjugated and nonconjugated monomers.



Poly(acetylene-co-octenamer)

Figure 3.15. ADMET copolymerization of 2,4-hexadiene and 2,10-dodecadiene.

When molybdenum catalyst 1c was added to an equimolar mixture of 2,4-hexadiene 2 and 2,10-dodecadiene 9 and stirred for 24 h at 30 °C, a green powder of poly(acetylene-co-octenamer) 12 was obtained. Evidence for the formation of copolymer rather than a mixture of two homopolymers was shown by the ^{1}H NMR spectrum of the copolymer 12 (Figure 3.16). The resonance of the CH_2 group of octenamer connected to the polyacetylene segment was found at 2.0 ppm which was 0.1 ppm downfield of the CH_2 group in the regular octenamer chain. Copolymer 12 had a molecular weight of 1020 according to the integration of the ^{1}H NMR resonances. Gel permeation chromatography (GPC) showed a number average molecular weight of 1090.

Copolymer 12 was a block copolymer according to its ^{1}H NMR and UV spectra. The integration of resonances at 5.5 to 6.5 ppm in the ^{1}H NMR spectrum (Figure 3. 16) showed an average of 4 to 5 repeat units for acetylene segments. The UV spectrum of poly(acetylene-co-octenamer) 12 (Figure 3.17) confirmed that the polymer 12 was a block copolymer, not a random copolymer. The UV

absorption of copolymer 12 was very similar to that of pure polyacetylene from bulk polymerization of 2,4-hexadiene, except for a different distribution. The multiple UV absorptions of copolymer 12 represented repeat units from 3 to 8.

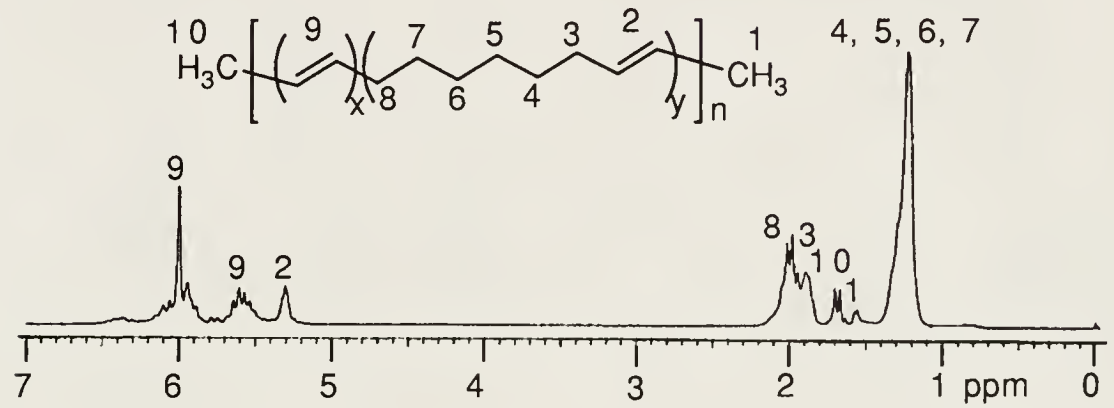


Figure 3.16. ^{1}H NMR spectrum of poly(acetylene-co-octenamer) 12.

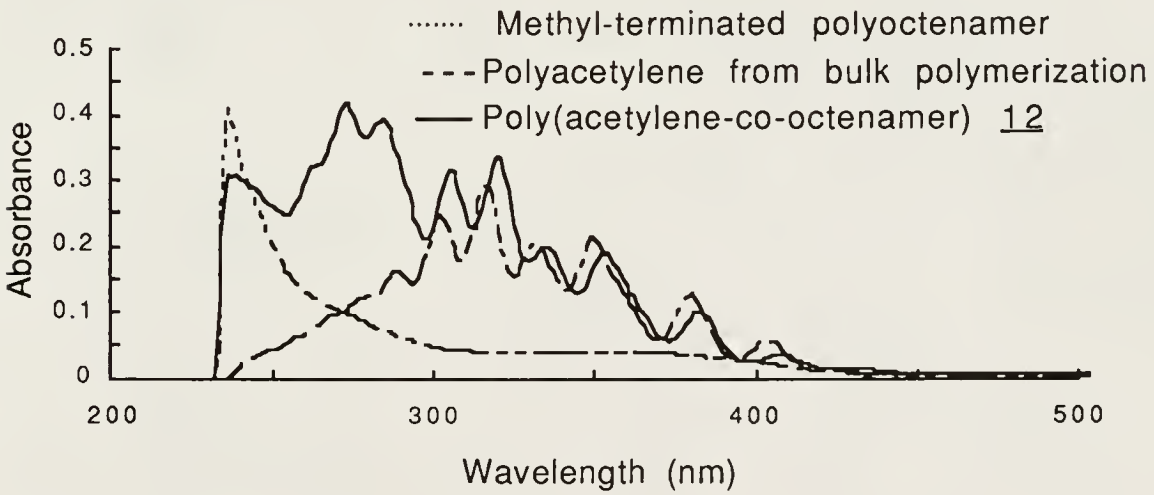


Figure 3.17. UV spectra of methyl-terminated polyoctenamer, bulk polymerization polyacetylene, and poly(acetylene-co-octenamer).

Poly(acetylene-co-octenamer) copolymers 13, 14, 15, and 16 were obtained from monomer feed ratios (mole ratio of 2,4-hexadiene to 2,10-dodecadiene), 1:2, 1:4, 2:1, and 4:1, respectively. Copolymer 13, 14, 15, and 16 had spectra and properties similar to those of copolymer 12 (ratio 1:1). They were block copolymers, and the molecular weight of the copolymer increased with increasing amounts of 2,10-dodecadiene in the monomer feed ratio (Table 3.3).

Table 3.3. Molecular weight of homopolymers and copolymers.

Polymer Number	Monomer Feed Ratio[a]	M_n ^1H NMR[b]	GPC Molecular Weight		
			M_n	M_w	M_w/M_n
3	1:0	290	490	700	1.4
16	4:1	670	530	660	1.2
15	2:1	730	560	660	1.2
12	1:1	1020	1090	1430	1.3
13	1:2	1500	1420	2130	1.5
14	1:4	1340	1580	2450	1.5
10	0:1	2860	2450	3180	1.3

[a]Monomer feed ratio refers to 2,4-hexadiene to 2,10-dodecadiene.
[b]M_n was obtained from the integration of ^1H NMR spectra.

The formation of block rather than random copolymers is due to the different reactivities of monomer 2,4-hexadiene 2 and 2,10-dodecadiene 9. It is suggested that, in the mixture of monomer 2 and 9, polyacetylene segments were formed first, then connected with polyoctenamer segments to produce a block copolymer.

Conclusions

Methyl-terminated polyacetylene oligomers can be successfully synthesized through the ADMET polymerization of conjugated internal dienes and trienes, such as 2,4-hexadiene and 2,4,6-octatriene, respectively. Solution polymerization of 2,4-hexadiene produced longer polyacetylene chains than did bulk polymerization of 2,4-hexadiene. Terminal dienes and trienes, 1,3-butadiene and 1,3,5-hexatriene, are not productive in ADMET polymerization, because they decompose the molybdenum catalyst.

Block poly(acetylene-co-octenamers) can be synthesized through ADMET copolymerization of an internal conjugated diene, 2,4-hexadiene, and an internal nonconjugated diene, 2,10-dodecadiene. An attempt to copolymerize 2,4-hexadiene and 1,9-decadiene is not successful, because 1,3-butadiene is generated through a metathesis exchange reaction between 2,4-hexadiene and 1,9-decadiene, and the newly formed 1,3-butadiene thus decomposes the Schrock's catalyst.

CHAPTER 4

SYNTHESIS OF TELECHELIC POLYACETYLENES THROUGH ADMET POLYMERIZATION

The term "telechelic polymer" was proposed in 1960 by Uraneck *et al.* to designate relatively low molecular weight macromolecules possessing two reactive functional groups situated at both chain ends.[163] The term originates from the Greek words *telos* "far" and *chelos* "claw," thus describing the molecule having two claws far away from each other, i.e., at the extremities of the chain, able to grip something else. Today's term "telechelic polymer" can apply to three reactive end-groups (tritelechelic polymer) or one reactive end-group (monotelechelic polymer).

Great interest in telechelic polymers exists because such polymers can be used to make block and graft copolymers. They also can be employed to form networks by using multifunctional linking agents or by being used in the so-called "liquid polymer" technology for reaction-injection modeling.

Almost all classical synthetic methods for the preparation of polymers have been used for the production of telechelic polymers, such as step polymerization, ionic polymerization, radical polymerization, ring-opening polymerization, and chain scission

reactions. Among them, step, condensation polymerization has been one of the most convenient methods to produce telechelic polymers.

Since methyl-terminated polyacetylene oligomers were successfully obtained from ADMET step polymerization, the character of the polymer and polymerization chemistry has led to the extension of the research to the synthesis of telechelic polyacetylene. This functionalized prepolymer could be used in the synthesis of segmented polyacetylene multiphase copolymers. The reaction chemistry of synthesizing telechelics was attractive for further study of the characteristics of ADMET polymerization. In this chapter, the polymerizabilities of functional group-terminated butadienes, and the reaction of 2,4-hexadiene with functionalized monoolefins were studied. The different reactivities between terminal monoolefins and internal monoolefins with 2,4-hexadiene also were investigated.

Polymerizabilities of Functional Group-Terminated 1,3-Butadienes

The successful synthesis of methyl-terminated polyacetylene oligomers via the ADMET polymerization of 2,4-hexadiene led to exploring the polymerizabilities of the functional group-terminated butadienes. Polymerization of such monomers was expected to produce telechelic polyacetylenes with perfect difunctionality (Figure 4.1).

Figure 4.1. The expected synthesis of telechelic polyacetylene from functional group-terminated butadiene.

Two commercially available functional group-terminated butadiene monomers, *cis,cis*-1,4-dicyano-1,3-butadiene 17 and *trans,trans*-1,4-diphenyl-1,3-butadiene 18, were selected to examine their polymerizability in ADMET polymerization. These two monomers were white crystals at room temperature. Attempted polymerizations were conducted in benzene solution (0.1 M) using molybdenum catalyst 1c (Figure 4.2). After the reaction mixture was stirred at room temperature for 48 h, benzene was evaporated and the remaining solid was characterized by NMR spectroscopy. The NMR spectra did not show trace of telechelic polymers for attempted polymerization of both monomers 17 and 18.

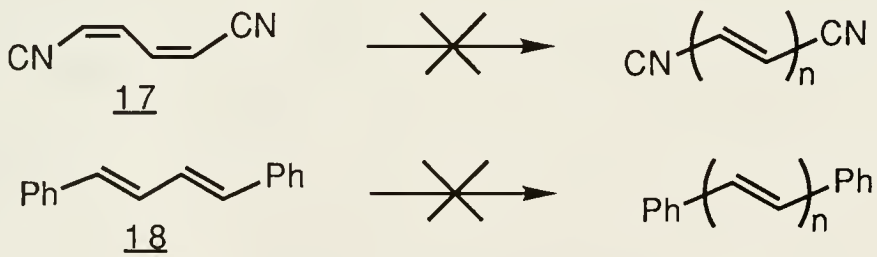


Figure 4.2. Attempted polymerization of *cis,cis*-1,4-dicyano-1,3-butadiene 17 and *trans,trans*-1,4-diphenyl-1,3-butadiene 18.

NMR studies were performed to obtain the details of these two non-productive ADMET polymerization reactions. 20.5 Mg (0.1 mmol,

2.5 equiv. of catalyst) of *trans,trans*-1,4-diphenyl-1,3-butadiene, 28 mg (0.04 mmol) of molybdenum catalyst, and 0.5 mL of C_6D_6 were mixed and sealed in a NMR tube. The sample was then characterized by NMR spectroscopy at 0.5 h, 1 h, 5 h, and 20 h, and it was somewhat surprising that no trace reaction was observed during this period. The ^1H NMR spectrum (Figure 4.3) showed that the catalyst 1c and monomer 18 remained unreacted, and the proton resonance of the original molybdenaneophylidene was clearly displayed at 12.19 ppm and remained unchanged during the course of the experiment.

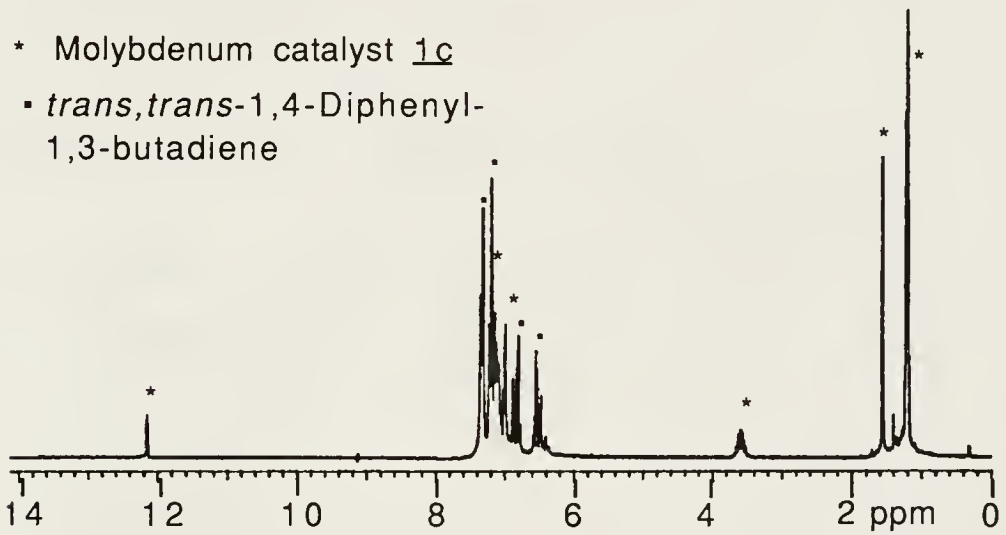


Figure 4.3. ^1H NMR spectrum of the mixture of *trans,trans*-1,4-diphenyl-1,3-butadiene and molybdenum catalyst 1c at room temperature.

Steric hindrance has been proposed as an explanation for the inactivity of monomer 18. The 4-coordinate imido/neophylidene complex has a pseudotetrahedral structure (Figure 4.4), in which the essentially linear imido and neophylidene ligands are *cis* to one another.[114] The 2-phenyl-propanyl group points toward the imido

ligand (*syn* orientation), and the two oxygen atoms of the alkoxy ligands are tipped away from the Mo=C and Mo=N multiple bonds. These four bulky ligands allow relatively small substrates to attack the metal to give a 5-coordinate intermediate metallacyclobutane complex but prevent intermolecular reaction from a large substrate. The linear conjugated molecule *trans,trans*-1,4-diphenyl-1,3-butadiene 18 is too large to access the metal center to form cyclobutane. Therefore the reaction between monomer 18 and catalyst 1c was hindered, and no change was observed in the NMR spectrum.

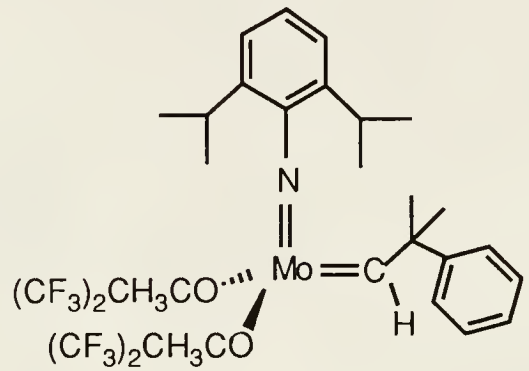


Figure 4.4. The pseudotetrahedral structure of molybdenum catalyst.

Unlike *trans,trans*-1,4-diphenyl-1,3-butadiene, *cis,cis*-1,4-dicyano-1,3-butadiene 17 reacted clearly with the molybdenum catalyst 1c to a certain degree. New proton resonances were observed in the ^1H NMR spectrum of the mixture of compound 17 and catalyst 1c (Figure 4.5), and a new alkylidene appeared at 13.93 ppm in addition to the initial neophylidene at 12.19 ppm. Proton resonances in the alkoxy group $OCCH_3(CF_3)_2$ and in the aromatic

imido group N-2,6-$C_6H_4[CH(CH_3)_2]_2$ of the catalyst 1c were shifted downfield as well.

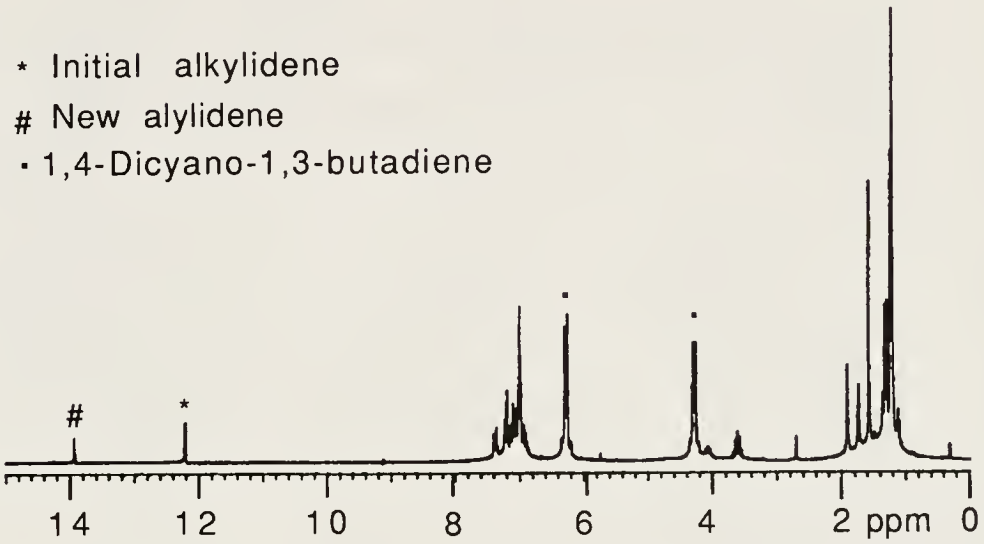


Figure 4.5. ^1H NMR spectrum for the sample of 6 h reaction between 1,4-dicyano-1,3-butadiene and molybdenum catalyst.

The new alkylidene signal (at 13.93 ppm) grew with increasing reaction time, while the initial neophylidene gradually decreased at room temperature. Equilibrium was reached after 6 h of reaction according to the time-traced NMR study. Figure 4.6 displays the change of new and original alkylidenes.

The shifts of NMR resonances of the molybdenum complex protons may be caused by the formation of a coordination complex between *cis,cis*-1,4-dicyano-1,3-butadiene 17 and the molybdenum catalyst 1c, where the nitrile group was coordinated with molybdenum atom (Figure 4.7). This proposed explanation was

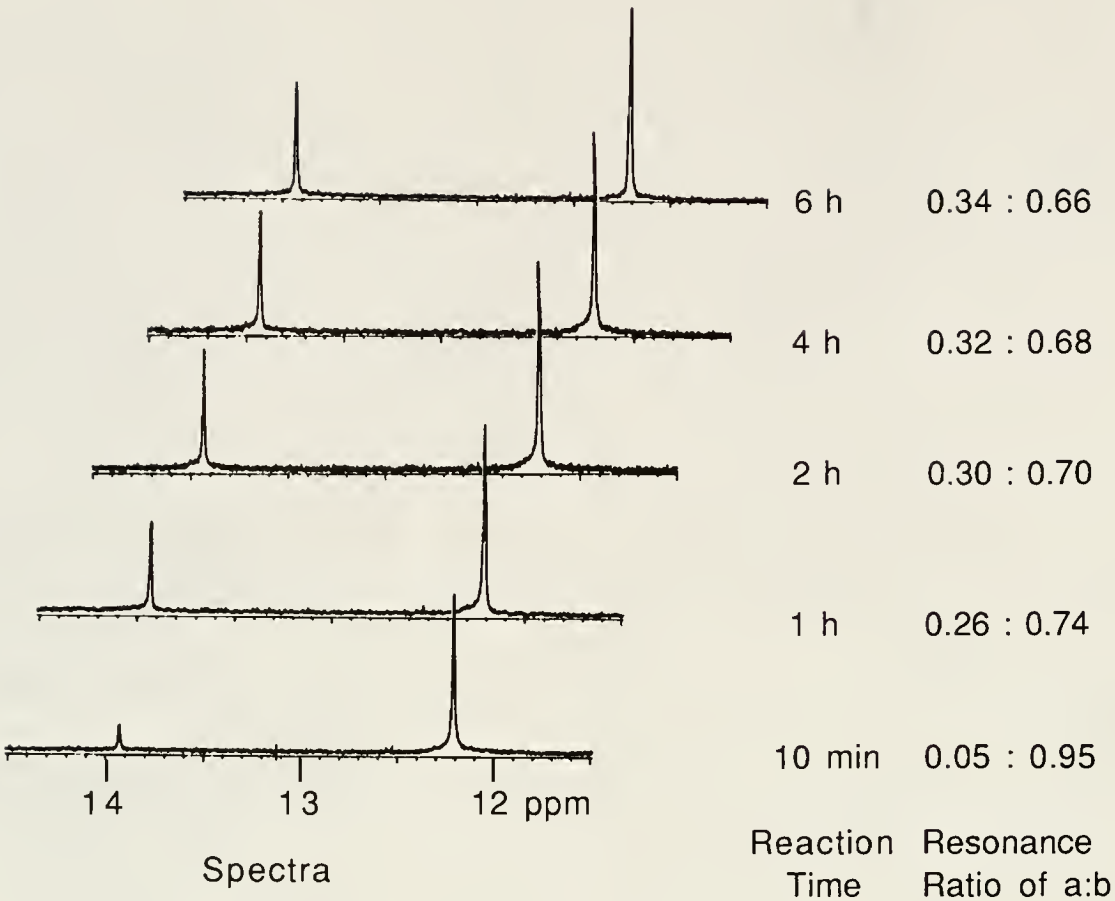


Figure 4.6. Alkylidene region of ^1H NMR spectrum (in C_6D_6) of reaction of *cis,cis*-1,4-dicyano-1,3-butadiene 17 (2 equiv. of 1c) and molybdenum catalyst 1c;
a: resonance of new alkylidene;
b: resonance of original neophylidene;
a:b: ratio of integration value for the two resonances.

supported by the observation of the similar shifts of NMR resonances for the molybdenum complex protons in the reaction of acetonitrile and the molybdenum catalyst.

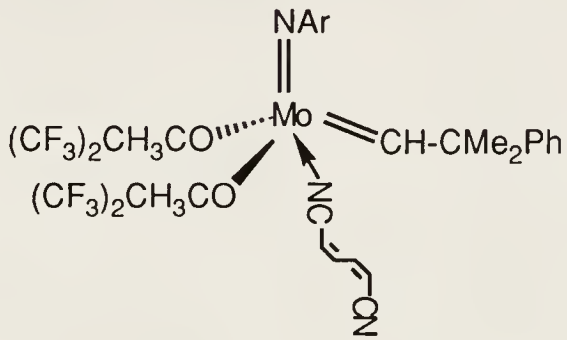


Figure 4.7. Possible coordination between *cis,cis*-1,4-dicyano-1,3-butadiene 17 and molybdenum catalyst 1c.

If the coordination between the nitrile group and molybdenum atom truly occurs, the proton resonances for *cis,cis*-1,4-dicyano-1,3-butadiene 17 should shift downfield as well. These shifts were not observed, however, and only initial resonances for compound 17 appeared in ^{1}H NMR spectrum.

The shift of the NMR resonances of molybdenum complex protons might also be caused by occurrence of a metathesis reaction between *cis,cis*-1,4-dicyano-1,3-butadiene 17 and molybdenum catalyst 1c (Figure 4.8). In this metathesis reaction, two alkylidenes, cyanomethylidene 59 and cyanovinyl alkylidene 60 (see Figure 4.8), could be formed. Other two products would be 1-cyano-5-methyl-5-phenyl-1,3-butadiene 61 and 1-cyano-3-methyl-3-phenyl-1-butene 62 (see Figure 4.8) which, however, could not be clearly identified in the ^{1}H NMR spectrum (Figure 4.5).

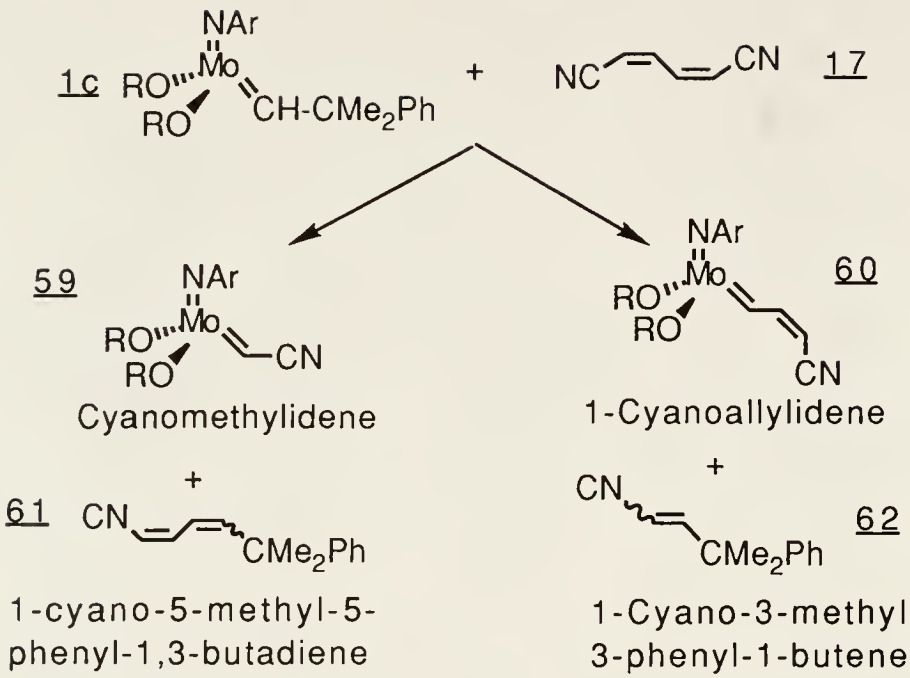


Figure 4.8. Formation of two alkylidenes in metathesis reaction of *cis,cis*-1,4-dicyano-1,3-butadiene 17 and molybdenum catalyst 1c.

It is also possible that an unknown reaction had occurred in the mixture of *cis,cis*-1,4-dicyano-1,3-butadiene 17 and molybdenum catalyst 1c. This unknown reaction might be responsible for the shift of proton NMR resonances of the catalyst 1c. Further study is needed to identify this reaction.

Attempted ADMET polymerization of *trans,trans*-1,4-diphenyl-1,3-butadiene and *cis,cis*-1,4-dicyano-1,3-butadiene was not successful, either because steric hindrance prohibited the ADMET reaction, or because a nonproductive reaction stopped ADMET polymerization.

A Model Study--
Synthesis of Telechelic Polymer through ADMET Polymerization of 1,9-Decadiene and a Monoolefin

Using a monofunctional reagent to terminate chain propagation and to control polymer molecular weight is well known in a step-growth reaction, and this general approach can be used in ADMET polymerization to produce telechelic polymers (Figure 4.9). When a functionalized monoolefin is added to a growing chain end, the propagation is stopped at this chain end, and this termination reaction continues until all molecule chains are ended by functionalized monoolefins.

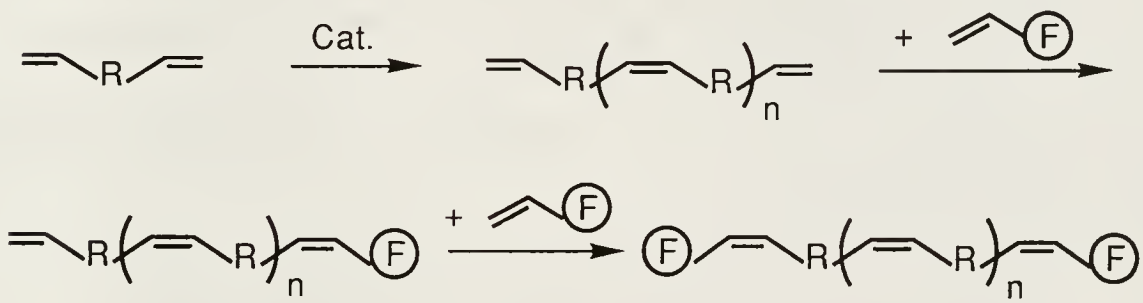


Figure 4.9. Formation of a telechelic polymer through ADMET polymerization of dienes and functionalized monoolefins.

1,9-Decadiene and 4-methyl-1-pentene were selected as a model system to study the feasibility of this process in ADMET polymerization, because these two compounds had moderate reaction rates and were without the negative neighboring group effect to complicate the reaction. An isobutyl-terminated polyoctenamer was

thus obtained through ADMET polymerization of 1,9-decadiene and 4-methyl-1-pentene using the molybdenum catalyst (Figure 4.10).

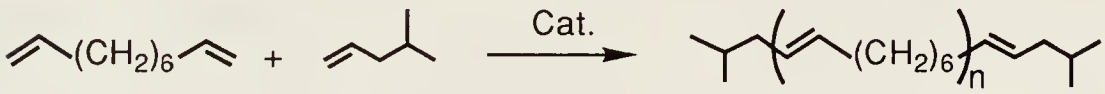


Figure 4.10. Synthesis of an isobutyl-terminated polyoctenamer through ADMET polymerization of 1,9-decadiene and 4-methyl-1-pentene

The ^{1}H NMR spectra of 1,9-decadiene, 4-methyl-1-pentene and isobutyl-terminated polyoctenamer (Figure 4.11) showed that the proton NMR resonances at 5.0 ppm and 5.8 ppm for terminal olefins of 1,9-decadiene had disappeared, and only the internal olefin resonance at 5.37 ppm was observed in the polymer spectrum. The presence of proton resonances of isobutyl group and the absence of the resonances of terminal olefin demonstrated that this polyoctenamer was capped by isobutyl groups at both ends.

According to the integration of the resonances in the ^{1}H NMR spectrum, the degree of polymerization (DP) for polymer 20 was 10, which was consistent with the 5:1 mole ratio of 1,9-decadiene to 4-methyl-1-pentene used in this reaction. The consistency between the actual value and the theoretical value of DP showed that the equilibrium was established in this ADMET polymerization. This result demonstrated that the telechelic polymer can be synthesized through ADMET polymerization of diene with monoolefin.

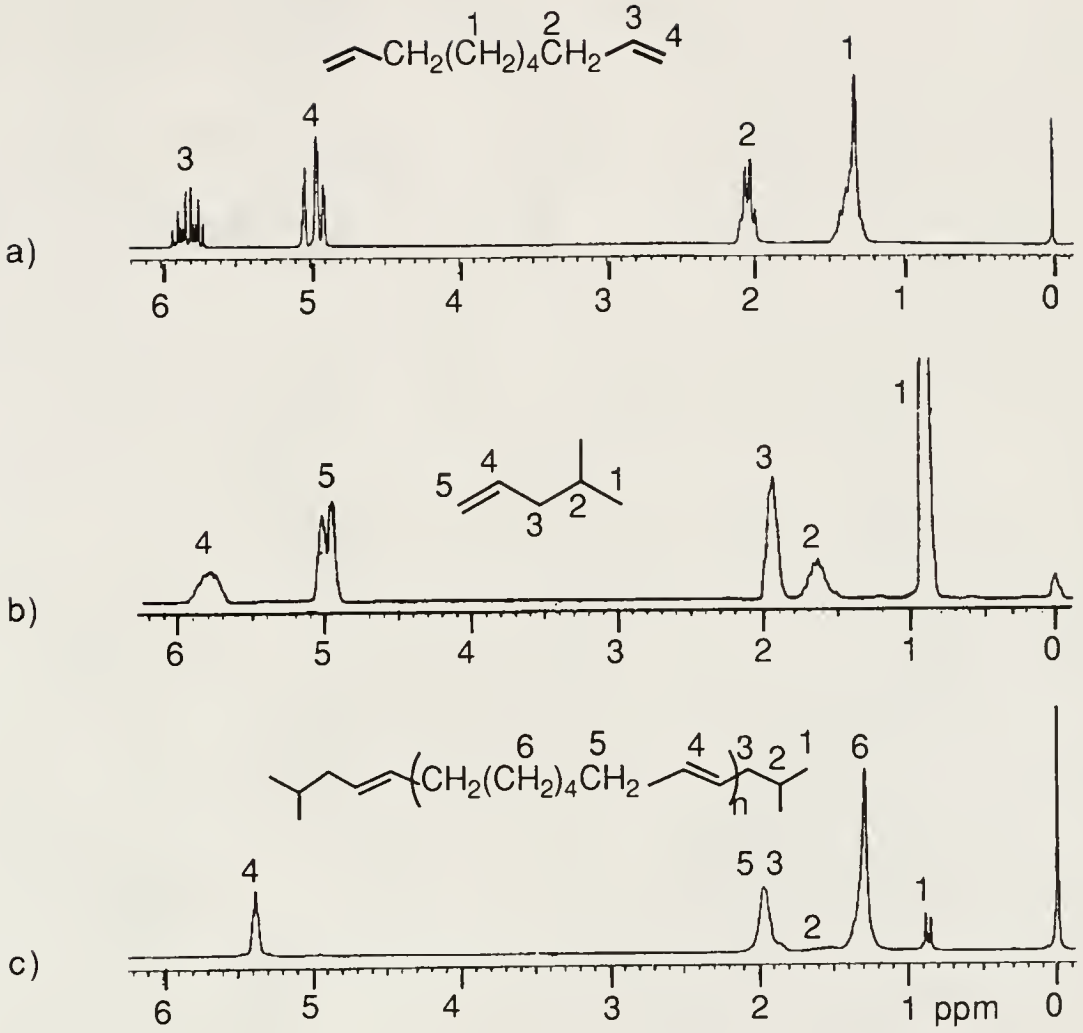


Figure 4.11. ^{1}H NMR spectra of a) 1,9-decadiene, b) 4-methyl-1-pentene, and c) isobutyl-terminated polyoctenamer.

The Reaction Between 2,4-Hexadiene and Terminal Monoolefins

Attempted polymerization of 2,4-hexadiene and 4-methyl-1-pentene using molybdenum complex as catalyst, a reaction similar to

the above polymerization of 1,9-decadiene and 4-methyl-1-pentene, was not successful. The reaction was observed in the first few minutes and then stopped.

The ^1H NMR spectrum of a liquid sample (distilled from above reaction mixture) showed that the liquid mainly contained starting materials, 1,9-decadiene and 4-methyl-1-pentene. In the mass spectrum of this liquid sample, however, three metathesis products, 3-methyl-3-phenyl-1-butene 63, 4-methyl-4-phenyl-2-pentene 64, and 2,7-dimethyl-4-octene 26, were found. These three products demonstrated that the metathesis reaction between 4-methyl-1-pentene, 2,4-hexadiene and the molybdenum catalyst had occurred initially (Figure 4.12).

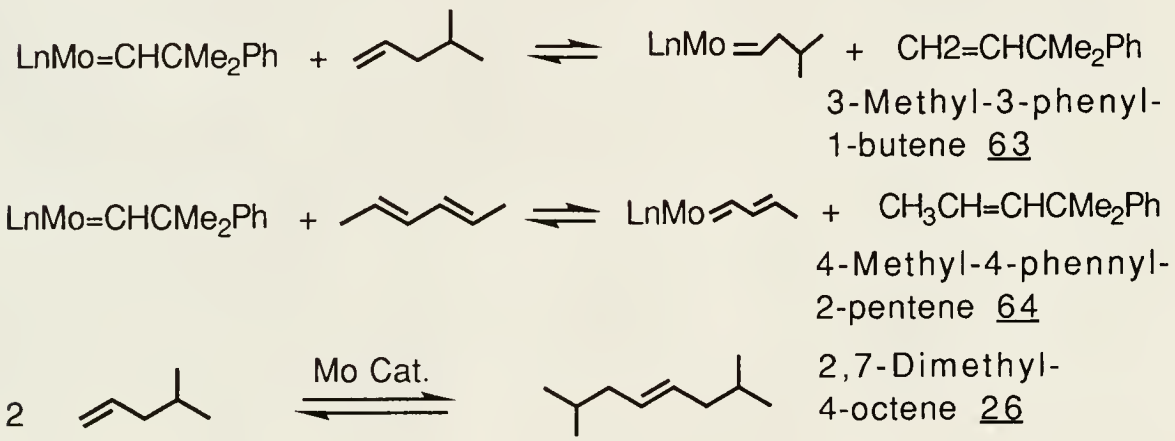


Figure 4.12. Equations represent formation of three metathesis products found in the mass spectrum.

The ^1H NMR spectrum of the solid sample (Figure 4.13), displayed that a tiny amount of isobutyl-capped polyacetylene had been formed, which was represented by the resonances with the

mark "*" in Figure 4.13. It was not clear, however, why the polymerization did not continue.

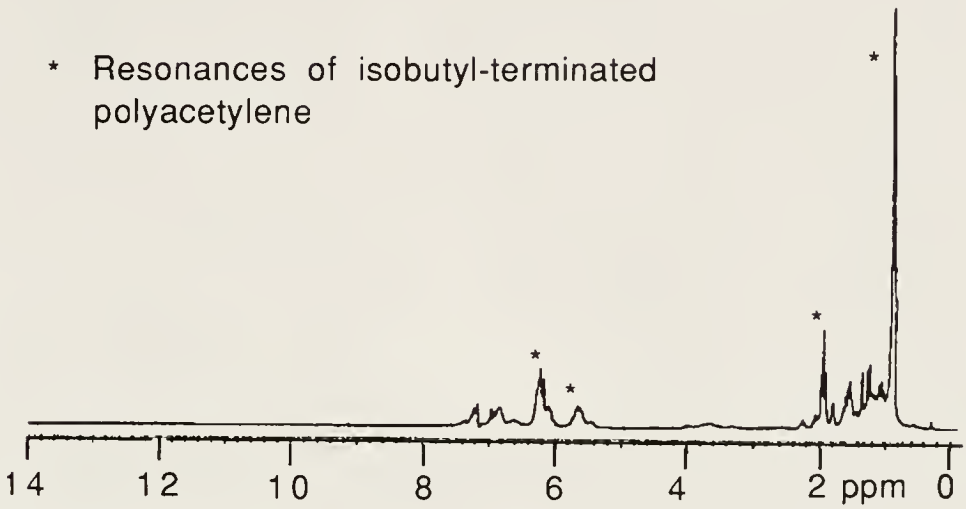


Figure 4.13. ^{1}H NMR spectrum of the solid sample from the reaction of 1,9-decadiene and 4-methyl-1-pentene using molybdenum catalyst.

An NMR reaction was carried out at room temperature to obtain more information on the reaction mechanism in the mixture of 2,4-hexadiene, 4–methyl-1-pentene, and the molybdenum catalyst. The proton and carbon resonances were collected at reaction time of 0.25 h, 0.50 h, 1 h, 7 h, and 24 h, respectively. The ^{1}H NMR spectra showed that the neophylidene resonance completely disappeared at initial time, and resonances at 6.0-6.2 ppm for conjugated double bond of polyacetylene appeared. The conjugated double bond, however, did not keep growing with reaction time.

According to the NMR spectra obtained at different times, the catalyst had obviously decomposed with increasing time. Again, 1,3-butadiene is formed via metathesis reaction between 2,4-

hexadiene and 4-methyl-1-pentene, and the newly formed 1,3-butadiene decomposes the catalyst.

There are two main competing reactions in a mixture of 2,4-hexadiene, 4-methyl-1-pentene, and the molybdenum catalyst: the formation of isobutyl-terminated polyacetylene and formation of 1,3-butadiene. The former is a productive reaction, but the latter decomposes the catalyst. A tiny amount of telechelic polymer was obtained in the mixture, since the formation of 1,3-butadiene and decomposition of the catalyst took some time. When the mole ratio of molybdenum catalyst to 2,4-hexadiene increased up to 1:50 (regular ratio is 1:300), isobutyl-terminated polyacetylene was produced in a 27% yield. This experimental result supports the hypothesis that the catalyst decomposition is not caused by the starting materials but by the reaction intermediates 1,3-butadiene.

Attempted polymerization of 2,4-hexadiene with other functionalized terminal monoolefins, such as allyltrimethylsilane and 4-penten-1-yl acetate, were also not successful. These experimental results confirmed that terminal monoolefins could not be used in the synthesis of telechelic polyacetylenes.

Investigation on the "Negative Neighboring Group Effect" in Metathesis Coupling Reactions

A "negative neighboring group effect" has been observed in the previous ADMET polymerization research.[153-155] Such studies demonstrated that ADMET polymerization did not occur for those

monomers, in which a functional group either was next to the dienes or had only one or sometimes two methylene spacers to dienes. These functional group-containing monomers deactivated Schrock's catalysts via certain coordination with the metal center. Several examples of such monomers are shown in Figure 4.14.

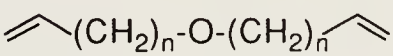
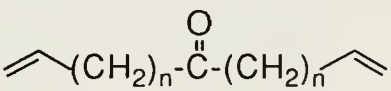
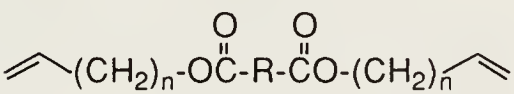
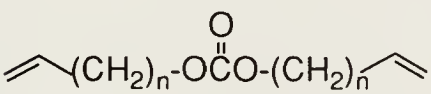
Monomer Structure	Polymerizability		
	n=0, 1	n=2	n>2
	No	Oligomer	Yes
	No	Yes	Yes
	No	Yes	Yes
	No	Yes	Yes

Figure 4.14. The relation between polymerizability and number of methylene spacers in monomers.

The "negative neighboring group effect" was also observed in metathesis coupling reaction in this research. Since most functionalized internal monoolefins used in the synthesis of telechelic polyacetylene were not commercially available, they were synthesized through a metathesis coupling reaction of allylic compounds. Allyl chloride, allyl amine, and 5-hexen-2-one have been tested and were found to be inactive in the coupling reaction (Figure 4.15).

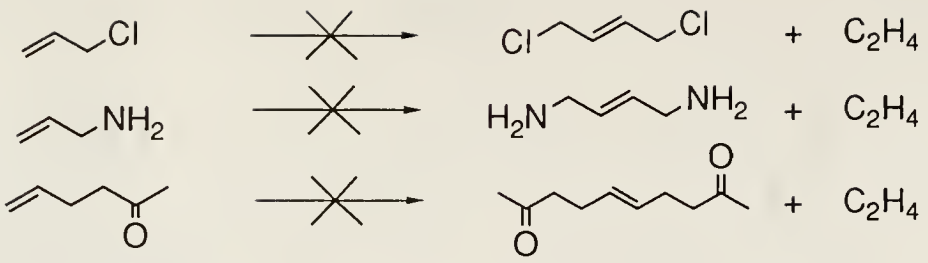


Figure 4.15. Attempted metathesis coupling of allyl chloride, allyl amine, and 5-hexen-2-one.

All these metathesis inactive functionalized monomers and monoolefins contain heteroatoms. These heteroatoms have lone electron pairs and are located in group VA, VIA and VIIA in the periodical table. A basic explanation for the lack of reactivity in ADMET polymerization[154,155] is that the heteroatom might coordinate to the catalyst metal center to form a stable metallacycle and thus prevent productive metathesis reaction (Figure 4.16).

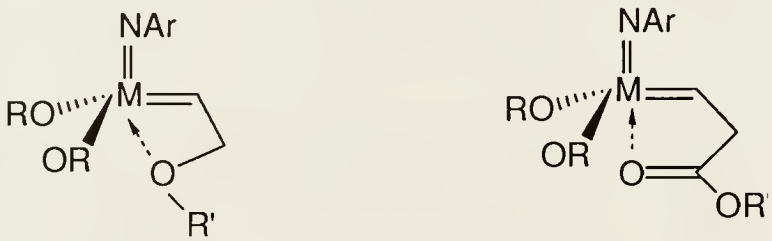


Figure 4.16. Formation of metallacycle of ether and ester with metal center preventing further metathesis reaction.

Schrock *et al.*[165] reported that the reaction between catalyst W(CH-t-Bu)(NAr)[$OCMe_2(CF_3)_2$]$_2$ 65 and a functionalized monoolefin, methyl acrylate, proceeded rapidly to give metallacyclobutane W[CH(t-Bu)CH_2CH(CO_2Me)](NAr)[$OCMe_2(CF_3)_2$]$_2$ 66 (Figure 4.17) in

high yields as a crystalline solid. Molybdenum catalyst Mo(CH-t-Bu)(NAr)($OCMe_2(CF_3)_2$]$_2$ 67 reacted with N,N-dimethylacrylamide to give metallacycle complex 68 which was analogous to 66.

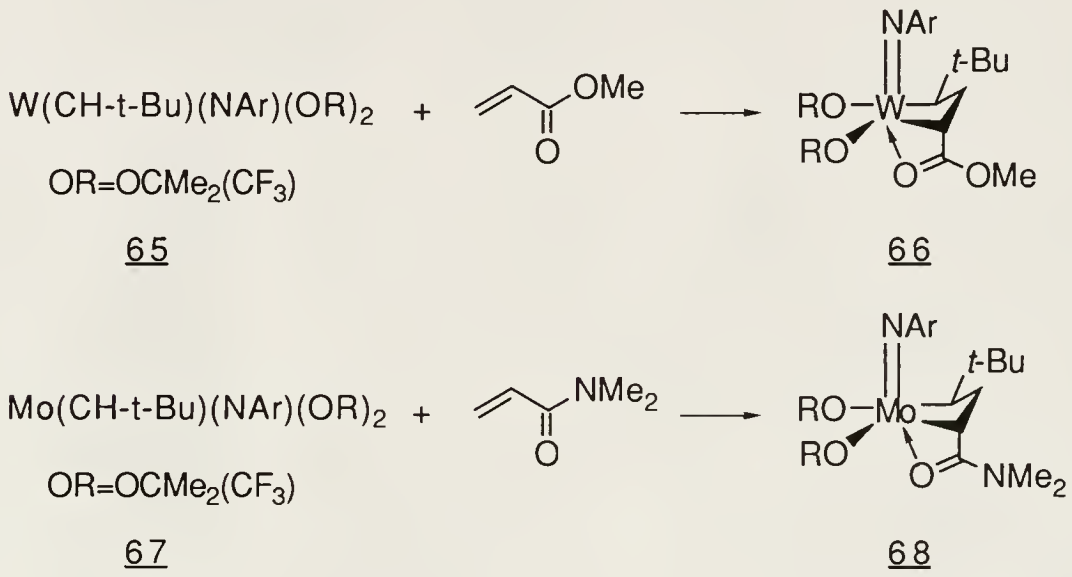


Figure 4.17. Reaction of neopentylidene complexes with methyl acrylate and N,N-dimethylacrylamide.[165]

According to this study, the inactive functionalized monoolefins in the metathesis coupling reaction appeared to have a different reaction mechanism from the literature reported above. This was because different catalysts were used. Molybdenum catalyst 1c, W(CH-CMe_2Ph)(NAr)[$OCMe(CF_3)_2$]$_2$, applied in the coupling reaction contained alkoxy of the type $OCMe(CF_3)_2$, which was a stronger electron withdrawing group than $OCMe_2(CF_3)$ in catalyst 67. Subsequently molybdenum catalyst 1c was more reactive than catalyst 67.

The room temperature ^1H NMR spectrum (Figure 4.18) of the reaction of allyl chloride with catalyst 1c was complicated,

however, it clearly showed that the metathesis exchange reaction between neophylidene and allyl chloride had occurred, since the chemical shifts at 6.0 ppm for the sp^2 protons of compound 63 (Figure 4.19, step A2) were found. No alkylidene resonances were displayed in the ^1H NMR spectrum, which demonstrated that the chloroethylidene 70 (Figure 4.19) is not as stable as the compounds proposed in Figure 4.16. The newly formed chloroethylidene 70 then reacted with another allyl chloride to form two possible metallacyclobutanes 71 and 72 through steps A3 and A5. Since no coupling product was produced in this reaction, step A4 did not occur. The compounds 71 and 72 might be stable enough to stop the further metathesis reaction and be responsible for non-productive reaction.

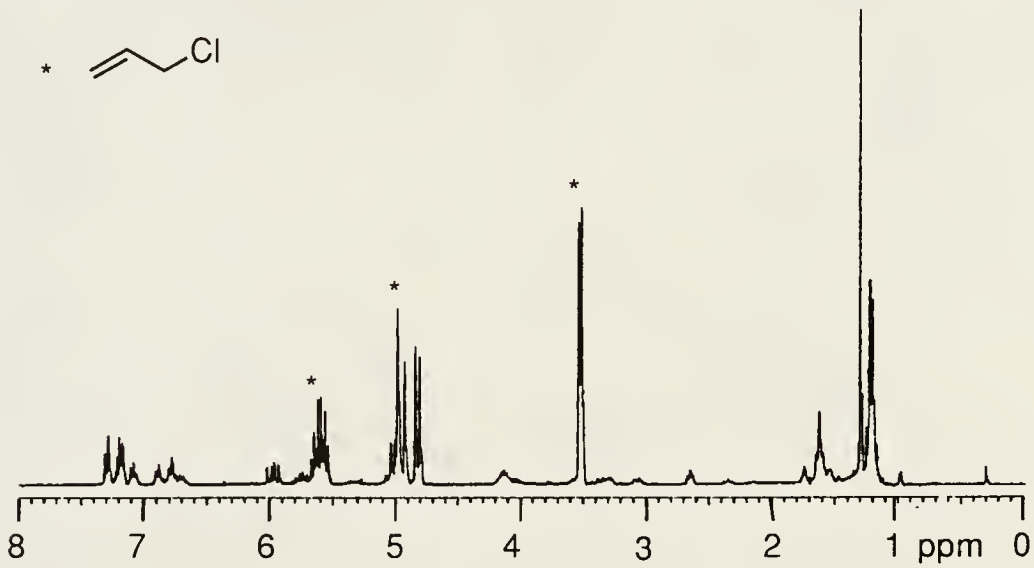


Figure 4.18. ^1H NMR spectrum of 30 min reaction of molybdenum catalyst 1c and allyl chloride.

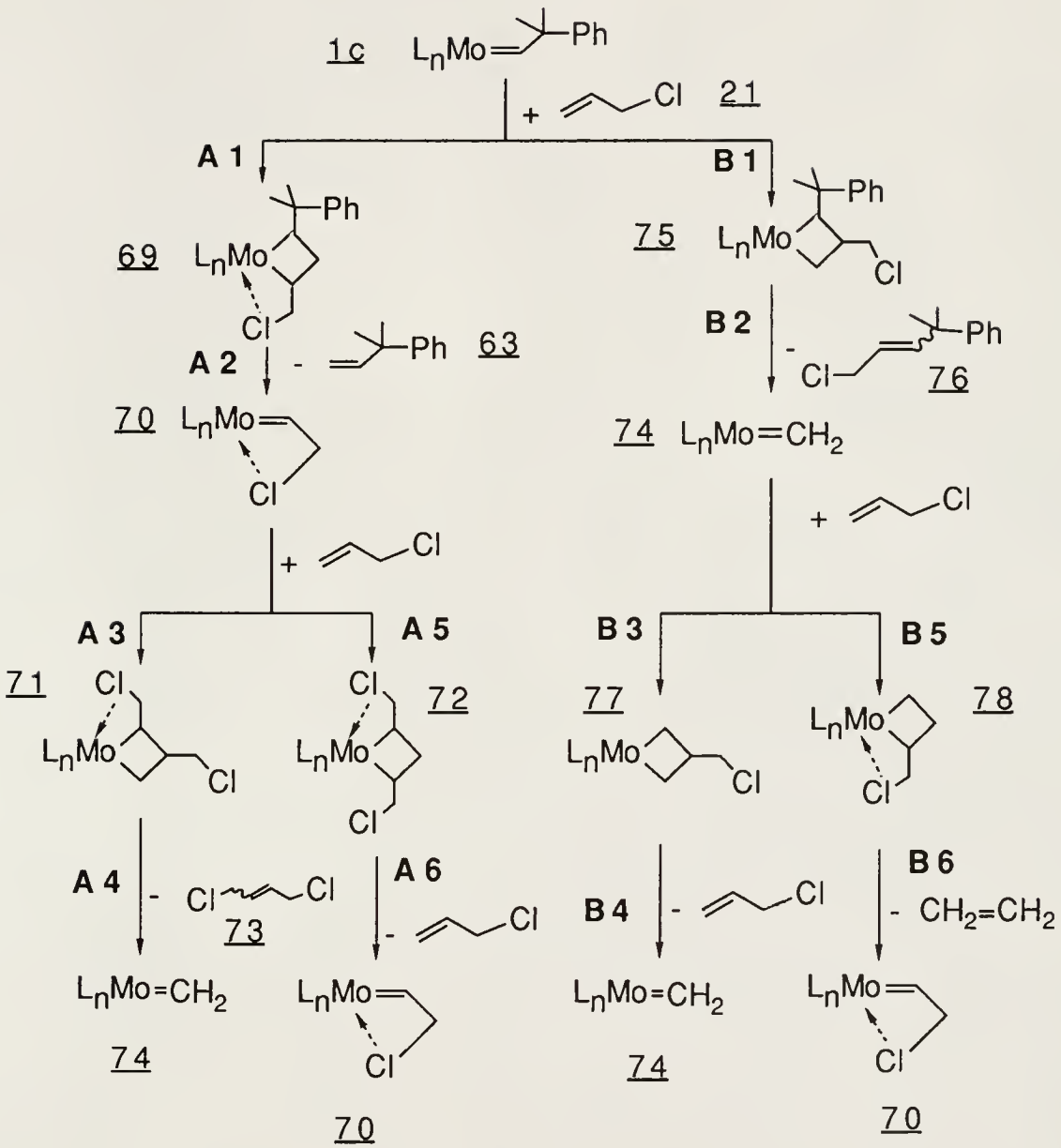


Figure 4.19. A scheme describes the possible reaction routes and products for the reaction of molybdenum catalyst 1c and allyl chloride. L_n represents ligands of NAr and OR.

The reaction route B in Figure 4.19 cannot be completely excluded. From the ^1H NMR spectrum in Figure 4.18, it is not clear whether the 1-chloro-4-methyl-4-phenyl-2-pentene 76 (see Figure 4.19) had formed. If, however, the reaction route B had occurred, the final product would be chloroethylidene 70 (Figure 4.19), which still led to route A to form compounds 71 and 72, and thus stops further metathesis reaction.

The NMR study for monoolefins 5-hexen-2-one and 3-butenal-diethyl-acetal were performed, and similar results were observed. Since the molybdenacyclobutane 72 had not been isolated, the above mechanism is only a proposal.

Successful coupling products, 2,7-dimethyl-4-octene 26, 4-octen-1,8-diyl acetate 28, and 1,4-bis(trimethylsilyl)-2-butene 30 were obtained quantitatively through metathesis coupling of 4-methyl-1-pentene 19, 4-penten-1-yl acetate 27, and allyltrimethylsilane 29, respectively (Figure 4.20).

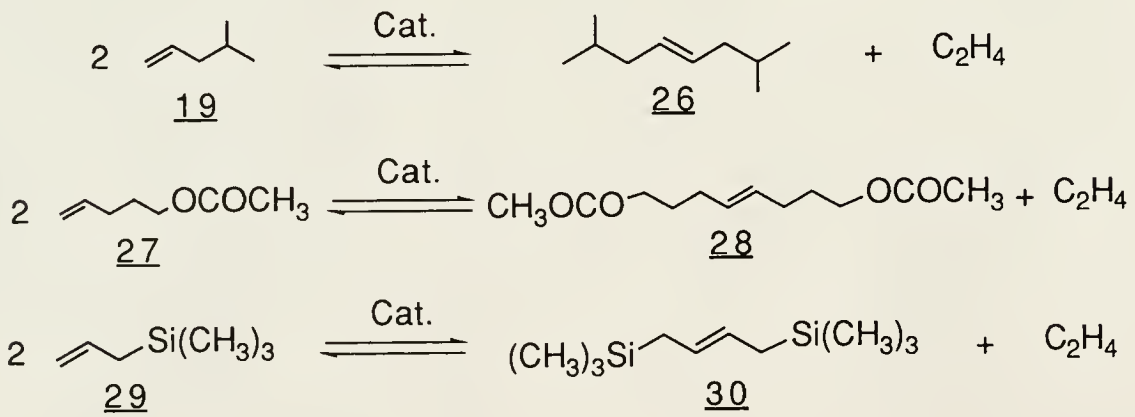


Figure 4.20. Metathesis coupling of 4-methyl-1-pentene 19, 4-penten-1-yl acetate 27, and allyltrimethylsilane 29.

Synthesis of Telechelic Polyacetylenes Through ADMET Polymerization of 2,4-Hexadiene and Internal Monoolefins

Internal monoolefins were used in the synthesis of telechelic polyacetylenes in order to avoid forming 1,3-butadiene and thus decomposing the catalyst. Hexyl-terminated polyacetylene 32 (Figure 4.21) was first successfully synthesized through ADMET polymerization of 2,4-hexadiene 2 and 7-tetradecene 31 using molybdenum catalyst 1c. Figure 4.22 showed the ^{13}C NMR spectrum of hexyl-terminated polyacetylene as compared to those of 7-tetradecene and 2,4-hexadiene. The carbon resonances of methyl groups at the 2,4-hexadiene ends disappeared in the NMR spectrum of polyacetylene 32, as conjugated diene resonances became conjugated polyene resonances. The chemical shifts of the hexyl group were clearly shown in the spectrum of the polymer 32.

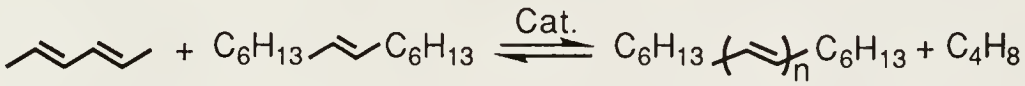


Figure 4.21. Synthesis of hexyl-terminated polyacetylene through ADMET polymerization of 2,4-hexadiene and 7-tetradecene.

The reactivity of the internal monoolefins with a methyl group at one end was also investigated. Polymerization of 2,4-hexadiene with 2-nonene and propenylbenzene using the molybdenum catalyst were completed, and the hexyl- and phenyl-terminated

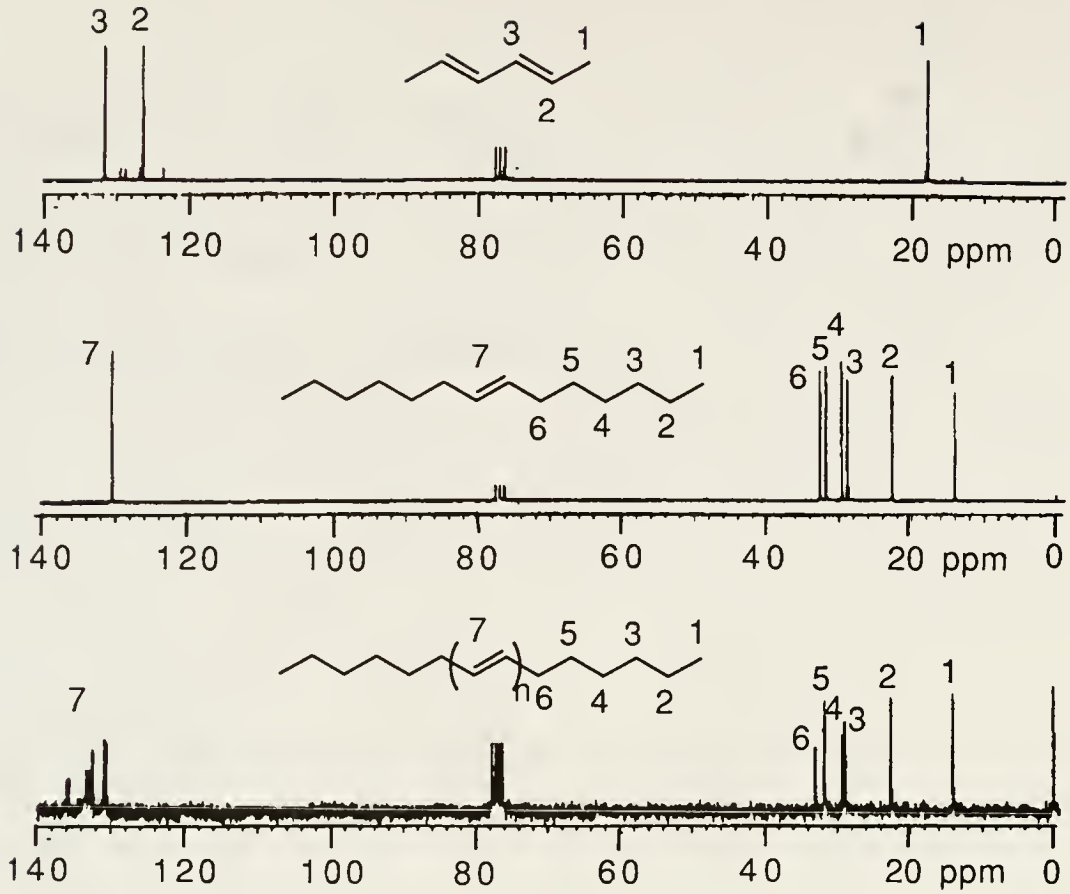


Figure 4.22. ^{13}C NMR spectrum of 2,4-hexadiene, 7-tetradecene, and hexyl-terminated polyacetylene.

polyacetylenes were obtained (Figure 4.23, (a), (b)). Trimethylsilyl- and 3-yl acetate-1-propyl-terminated polyacetylenes were synthesized through ADMET polymerization of 2,4-hexadiene with 1,4-trimethylsilyl-2-butene and 4-octen-1,8-diyl acetate, respectively (Figure 4.23, (c), (d)).

Table 4.1 lists the degree of polymerization (DP) and functionality of the telechelic polyacetylenes. The functionality represents the number of terminal functional groups in one

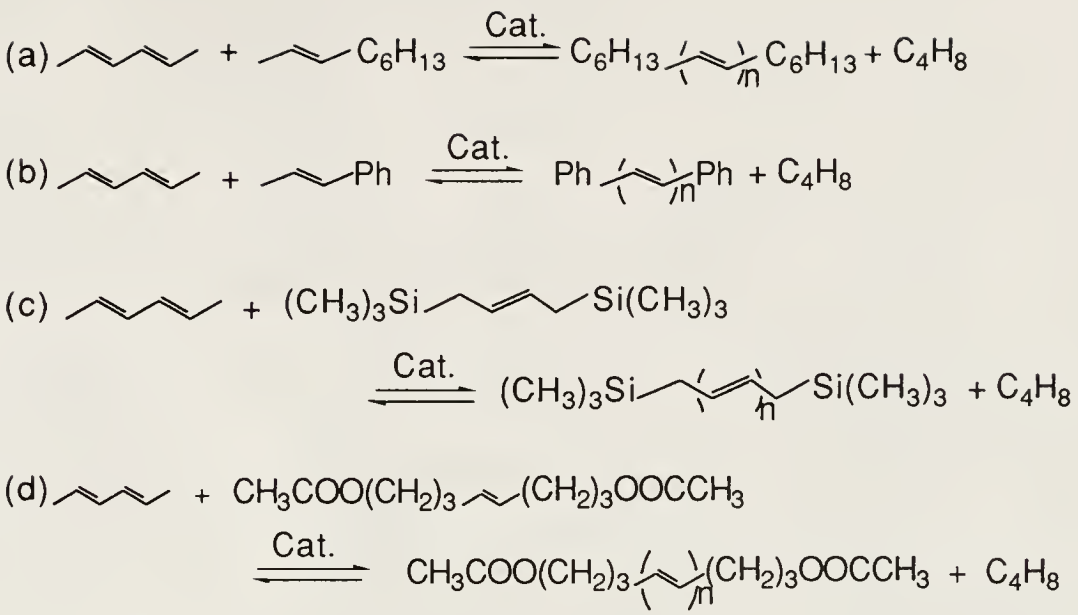


Figure 4.23. Telechelic polyacetylenes obtained from ADMET polymerization of 2,4-hexadiene and internal monoolefins.

telechelic macromolecule. A polymer molecule capped by two functional groups at both ends has a functionality of two, and a polymer capped by one functional group has a functionality of one. The average functionality for a telechelic polyacetylene was calculated from integration of the ^1H NMR resonances of the end functional group *versus* end methyl group. In a model study of the polymerization of 1,9-decadiene with 4-methyl-1-pentene, equilibrium was established, and thus the polyoctenamer was fully capped by isobutyl groups via removal of ethylene. In the synthesis of telechelic polyacetylenes, polyacetylene molecules were formed fast, and some of them were precipitated before they were fully capped by functional groups. Therefore the functionality of the telechelic polyacetylenes was lower than two.

Table 4.1. List of reagents ratio, degree of polymerization, and functionality for telechelic polyacetylenes.

Monoolefins	Mole Ratio 2,4-Hexadiene : Monoolefins	Degree of Polymerization	Functionality
7-Tetradecene	4:1	7	1.9
2-nonene	2:1	8	1.6
Propenyl-benzene	2:1	7	1.4
1,4-Bis(trimethyl-silyl)-2-butene	4:1	8	1.3
4-Octene-1,8-diyl Acetate	4:1	6	1.3

Conclusions

The successful synthesis of telechelic polyacetylenes was achieved through the ADMET polymerization of 2,4-hexadiene with internal monoolefins, such as 7-tetradecene, propenylbenzene, 1,4-bis(trimethylsilyl)-2-butene, and 4-octene-1,8-diyl acetate, respectively. The ADMET polymerization of functional group-terminated 1,3-butadienes was not successful, either because steric hindrance prohibited the ADMET reaction or because a non-productive reaction stopped ADMET polymerization. Telechelic polyacetylenes could not be synthesized through ADMET polymerization of 2,4-

hexadiene with terminal monoolefins, since the metathesis exchange reaction between 2,4-hexadiene and terminal monoolefin produced 1,3-butadiene, which then decomposed the metal alkylidene complexes.

CHAPTER 5

ADMET POLYMERIZATION AND COPOLYMERIZATION OF DIPROPENYLBENZENES

Dipropenylbenzenes are another type of conjugated monomer and consist of two internal olefins and a benzene ring in a molecule. While ADMET homopolymer and copolymers of 1,4-dipropenylbenzene have been examined in previous ADMET studies,[161] the research conducted here extended the scope of previous work to 1,2-dipropenylbenzene and 1,3-dipropenylbenzene. Their polymerization chemistry and different reactivities from 1,4-dipropenylbenzene were investigated. The random and block copolymers of poly(phenylenevinylene-co-octenamer) were synthesized, and the comparison of the reactivities between conjugated dienes and non-conjugated dienes were discussed.

ADMET Polymerization of 1,3-Dipropenylbenzene

The monomer 1,3-dipropenylbenzene 40 was synthesized by a Wittig reaction of commercially available isophthaldehyde and ethyltriphenylphosphonium bromide (Figure 5.1). The compound obtained through this one-step reaction showed three isomers, *trans,trans-*, *trans,cis-*, and *cis,cis-* isomers, because the monomer

contained two propenyl groups. Table 5.1 listed the calculated values of heat of formation and structure energy for the three isomers.

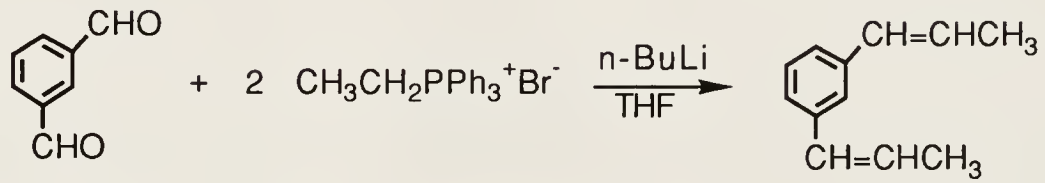


Figure 5.1. Synthesis of 1,3-dipropenylbenzene through Wittig reaction of isophthaldehyde and ethyltriphenyl-phosphonium bromide.

Table 5.1. The values of heat and structure energy for isomers of 1,3-dipropenylbenzene calculated through a molecular modeling program.

Configuration	Heat of Energy kcal/mol	Structure Energy kcal/mol
Trans,trans	33.4	16.2
Trans,cis	34.8	18.4
Cis,cis	36.3	20.3

Poly(1,3-phenylene vinylene) 42 was synthesized by mixing 6.3 mmol of 1,3-dipropenylbenzene with 0.025 mmol of tungsten catalyst 1b and stirring at room temperature for 30 min. Figure 5.2 showed the ^1H NMR spectrum of polymer 42. The proton resonance of the terminal methyl group was displayed at 1.84 ppm, and the resonances for two terminal vinylene protons were at 6.3 and 6.4 ppm. The resonances for vinylene between phenylene were displayed at 7.1 ppm.

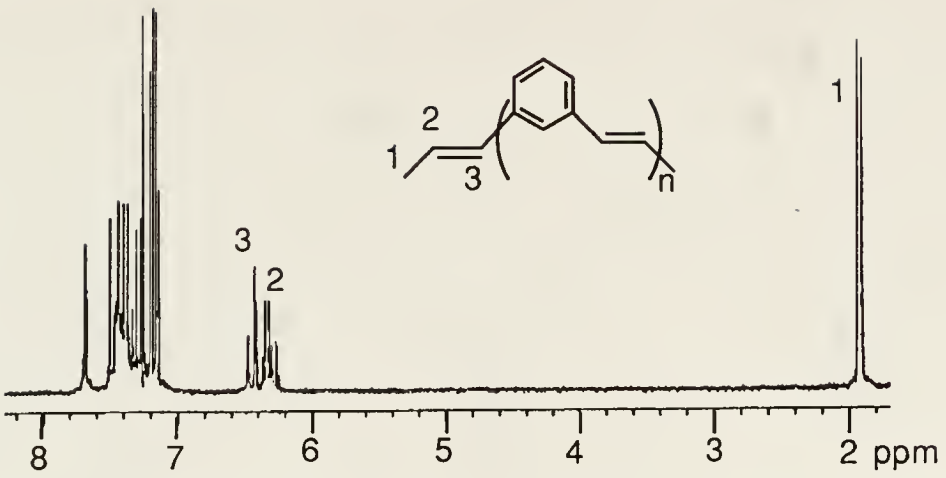


Figure 5.2. ^{1}H NMR spectrum of poly(1,3-phenylene vinylene).

According to the integration of the ^{1}H NMR spectrum, the average degree of polymerization of poly(1,3-phenylene vinylene) was 4, which was a low molecular weight oligomer. The reason for only producing oligomers in this step, condensation, equilibrium polymerization is that the conjugated oligomers had a regular configuration and were easily coagulated and precipitated from reaction system. In this manner, the terminal olefins of the oligomers were restricted from further metathesis condensation.

The UV absorbance of poly(1,3-phenylene vinylene) 42 was at the region of 235 to 350 nm, and λ_{max} were at 266 and 306 nm (Figure 5.3). The poly(1,3-phenylene vinylene) oligomer displayed shorter wavelength absorbance than the absorbance of poly(1,4-phenylene vinylene) 46.

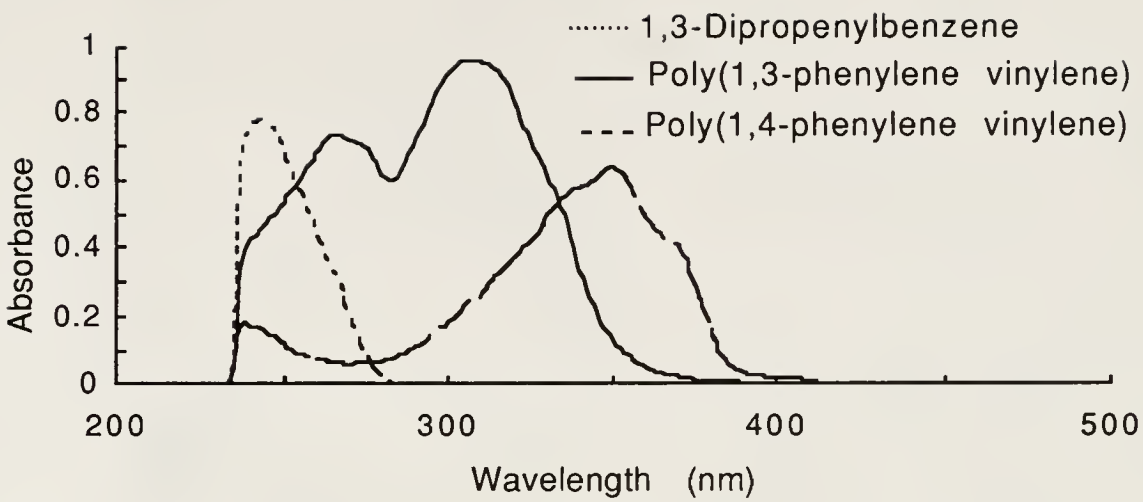


Figure 5.3. The UV spectra of 1,3-dipropenylbenzene, poly(1,3-phenylene vinylene), and poly(1,4-phenylene vinylene).

Three new alkylidene resonances were observed in the ^{1}H NMR spectrum (Figure 5.4) for the polymerization of 1,3-dipropenylbenzene. The new resonances were at 12.56 (*a*), 12.91 (*b*), and 12.95 (*c*) ppm, and the initial neophylidene resonance was at 12.15 ppm.

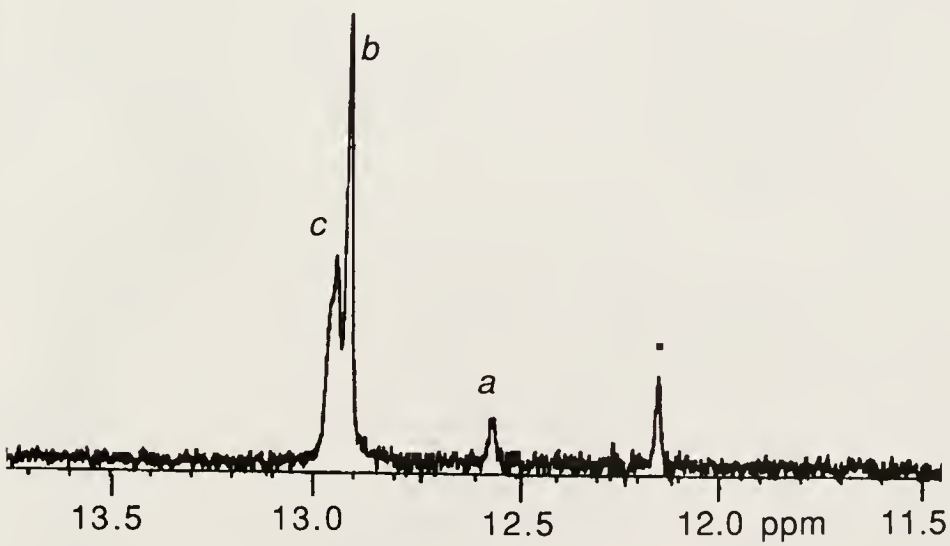


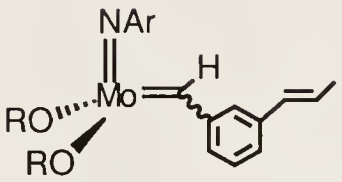
Figure 5.4. ^{1}H NMR spectrum of a 2 h reaction sample displayed new resonances (*a, b, c*) and initial resonance (▪).

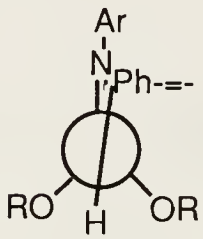
According to the literature reported by Schrock *et al.*,[126] an alkylidene (Figure 5.5, bottom) formed from the reaction of 7-oxanorbonadiene with a molybdenum catalyst having a *syn* resonance at 11.23 ppm (major) and *anti* resonance at 11.07 ppm (minor). The *anti* refers to the rotamer in which the alkylidene substituent points away from the imido nitrogen atom in psuedotetrahedral metal complex, and *syn* rotamer refers to the alkylidene substituent pointing towards the imido nitrogen atom. Rotamers are a consequence of the fact[116] that of the two orbitals that could be used to form a π bond between the metal and carbon, that which is perpendicular to the N-M-C plane is the most accessible; the d orbital that lies in the N-M-C plane probably is used primarily to form a second ("dative") π bond between the metal and the imido ligand. However an alkylidene ligand that is rotated by 90° can be stabilized by d orbital that lies in the N-M-C plane.

Three new resonances observed in the polymerization of 1,3-propenylbenzene (Figure 5.4) are attributed to the different alkylidenes and rotamers. The resonances *b* and *c* represent the rotamers of 3-propenylbenzylidene Mo(CH-1,3-C_6H_4-CH=$CHCH_3$)(NAr)[$OCCH_3(CF_3)_2$]$_2$ 75. The rotamers *A* (*syn*) and *B* (*anti*) in Figure 5.5 are the most accessible conformations, in which the π bond between the metal and carbon is perpendicular to the N-M-C plane. When the rotamer *A* was rotated by 90°, the conformation *C* was formed, but it is only a transition state and not stable enough to be detected by NMR spectroscopy. Since the resonance *a* appeared after 2 h reaction, it is more likely to be a

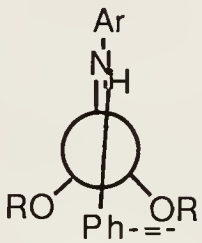
propagation chain alkylidene, Mo[CH-(-1,3-C_6H_4-CH=CH-)n-CH_3](NAr)[$OCCH_3(CF_3)_2$]2.

3-propenylbenzylidene and its rotamers

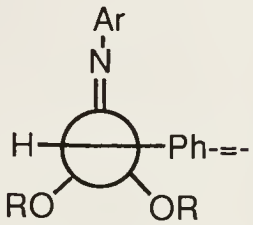




A (Syn)

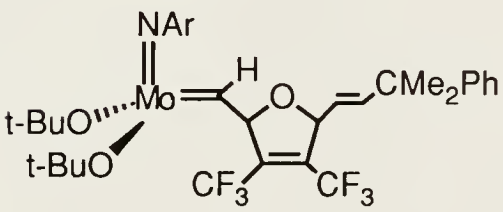


B (Anti)

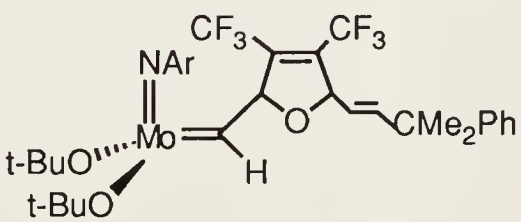


C (transition state)

Alkylidene reported in the literature[126]



Anti



Syn

Figure 5.5. View of the molybdenalkylidene complexes and the rotamers.

The new alkylidenes were relatively stable, but were still very reactive. Addition of another monomer or propagating chain to the new alkylidene formed a metallacyclobutane, which then rearranged to a higher molecular weight propagating chain. In this manner, the polymer product was produced.

ADMET Polymerization of 1,2-Dipropenylbenzene

Monomer 1,2-dipropenylbenzene 40 was synthesized by a Wittig reaction of phthalic dicarboxaldehyde and ethyltriphenylphosphonium bromide (Figure 5.6). The compound obtained was a mixture of *trans* (42%) and *cis* (58%) isomers. The heat of formation and structure energy of three isomers (*trans,trans, trans,cis*, and *cis,cis*) are listed in Table 5.5. 1,2-Dipropenylbenzene has a higher structure energy than 1,4-dipropenylbenzene and 1,3-dipropenylbenzene.

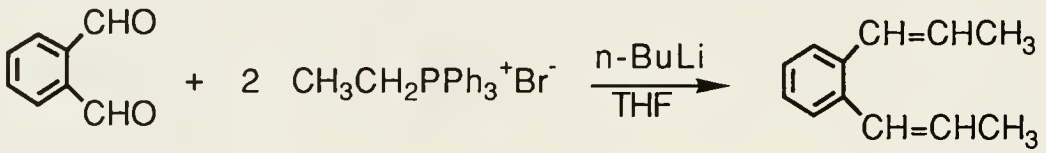


Figure 5.6. Synthesis of 1,2-dipropenylbenzene through Wittig reaction of phthalic dicarboxaldehyde and ethyltriphenylphosphonium bromide.

Table 5.2. The values of heat energy and structure energy for isomers of 1,2-dipropenylbenzene calculated through molecular modeling program.

Configuration	Heat of Energy kcal/mol	Structure Energy kcal/mol
Trans ,trans	33.9	19.0
Trans,cis	35.2	19.9
Cis,cis	37.0	21.5

When 6.3 mmol (250 equiv of catalyst) of 1,2-dipropenylbenzene was mixed with 0.025 mmol of tungsten catalyst 1a and stirred at room temperature, the solution first exhibited a red color and then gradually became dark black in 2 h. No ADMET polymer was found after the solution was stirred at room temperature for one week. Only unreacted monomer was recovered in this reaction mixture.

The ADMET polymerization, however, was initiated, while the original mixture of 1,2-dipropenylbenzene (1 g) and tungsten catalyst (20 mg), was kept at room temperature for 6 weeks and was added in by another 20 mg of catalyst. After 48 h of stirring, solid poly(1,2-phenylene vinylene) was obtained. This successful ADMET polymerization suggested that, in the homopolymerization of 1,2-dipropenylbenzene, a larger amount of catalyst was needed for the production of a polymer. Different ratios of catalyst to monomer were tried, and 1 equiv of catalyst to 60 equiv of monomer (80 mg of catalyst 1a to 1 g of monomer 39) was necessary for successful synthesis of poly(1,2-phenylene vinylene).

Figure 5.7 showed the ^1H NMR spectra of monomer 39 and its polymer 41. Only *trans* configurations for the double bonds on the chain ends of the polymer 41 were observed. The *cis* configurations for the methyl protons and sp^2 protons in monomer 39 (see Figure 5.7) now have disappeared in polymer spectrum. The proton resonances for phenylene in the polymer are from 7.15 to 7.8 ppm, and proton resonances for double bonds between phenylene are around 7.2 ppm.

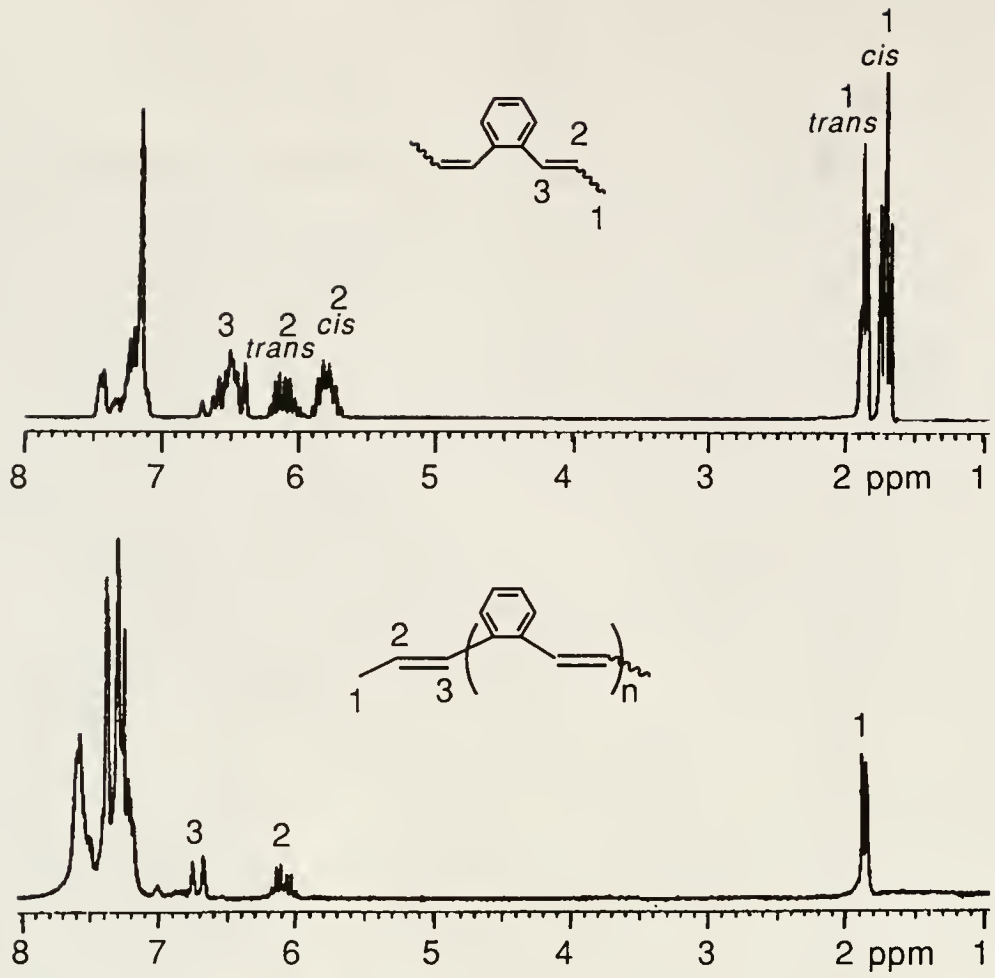


Figure 5.7. ^{1}H NMR spectra of 1,2-dipropenylbenzene and its polymer 41.

Compared with the fast homopolymerization of 1,4- and 1,3-dipropenylbenzene, polymerization of 1,2-dipropenylbenzene was slow and required a large amount of catalyst. The first step of the metathesis reaction between monomer 39 and the metal catalyst was the formation of 2-propenylbenzylidene 82 (Figure 5.8). This new alkylidene appeared remarkably stable, and further metathesis polymerization was so slow that the reaction actually was not productive when using a regular amount of catalyst.

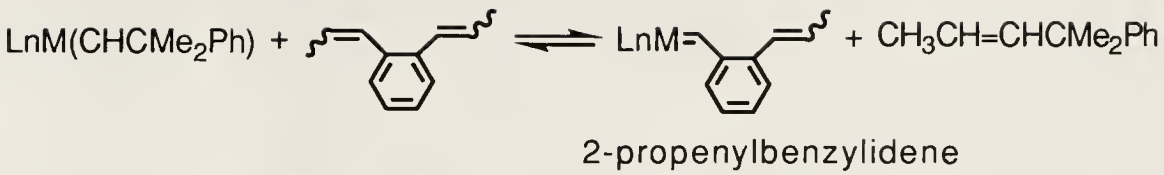


Figure 5.8. Formation of 2-propenylbenzylidene through metathesis exchange reaction.

Upon following this reaction by ^{1}H NMR at low monomer levels with molybdenum catalyst 1c (4 equiv monomer to 1 equiv catalyst), the resonances for newly formed alkylidenes were observed. The five new resonances in the ^{1}H NMR spectrum (Figure 5.9) ranged from 13.18 ppm to 13.52 ppm. The resonances *d* and *e* are proposed to be the *syn* and *anti* rotamers of the 2-propenylbenzylidene 82 (also see Figure 5.10). The resonances *a* and *c* might be attributed to either the different *trans* and *cis* configurations of the *ortho* propenyl group, or the limitation of the free rotation of the benzene ring by the interaction between the *ortho* propenyl group and large ligands of the metal (Figure 5.10). The resonance b, which appeared after 4 h reaction, represented the propagation chain alkylidene, Mo[CH-(-1,2-C_6H_4-CH=CH-)$_n$-CH_3](NAr)[$OCCH_3(CF_3)_2$]$_2$.

A very low reactivity of 1,2-dipropenylbenzene in ADMET polymerization had been observed. One argument is that steric hindrance prevents the condensation reaction with the second monomer. In newly formed 2-propenylbenzylidene, the *ortho* propenyl partially shields the front face of the alkylidene and

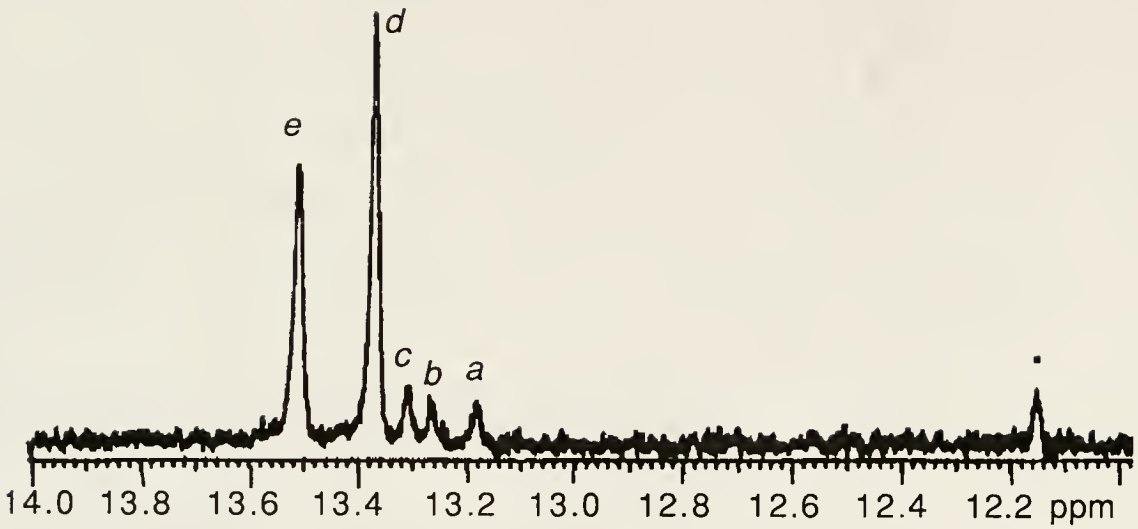
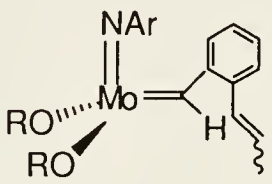
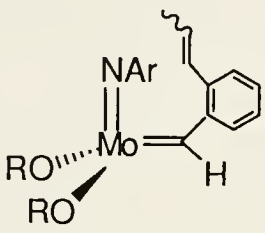


Figure 5.9. ^{1}H NMR spectrum of initial alkylidene resonance(▪) and five new (*a, b, c, d, e*) resonances.

Two *syn* rotamers

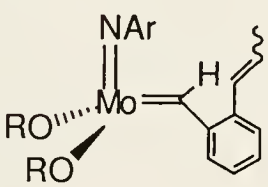


A

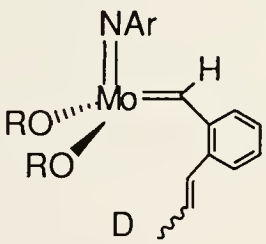


B

Two *anti* rotamers



C



D

Figure 5.10. The possible different *syn* and *anti* rotamers of 2-propenylbenzylidene complex.

prevents another dipropenylbenzene from accessing to form metallacyclobutane. Another argument is that the *ortho* propenyl itself attacks the alkylidene to form a relatively stable complex (Figure 5.11), which is in an equilibrium state. This intramolecular reaction may prevent the second monomer from effectively attacking the metal center and thus would greatly slow down the polymerization rate.

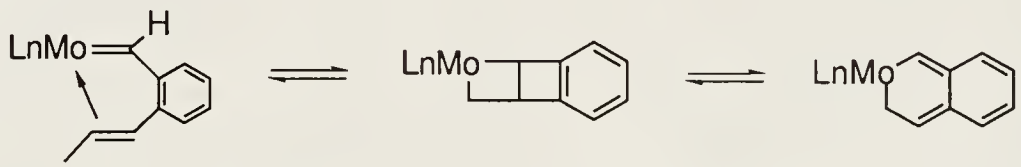


Figure 5.11. Formation of a complex by intramolecular metathesis reaction.

According to the integration of proton resonances, the average degree of polymerization of poly(1,2-phenylene vinylene) was 8, which was still a low molecular weight oligomer; however, the molecular weight of poly(1,2-phenylene vinylene) was higher than that of poly(1,3-phenylene vinylene) and poly(1,4-phenylene vinylene). The UV absorbance of poly(1,2-phenylene vinylene) (Figure 5.12) ranged from 235 to 400 nm, and the λ_{max} were at 278 and 328 nm. Even though polymer 41 had higher degree of polymerization than did poly(1,4-phenylene vinylene), the UV spectrum did not display a longer wavelength absorption.

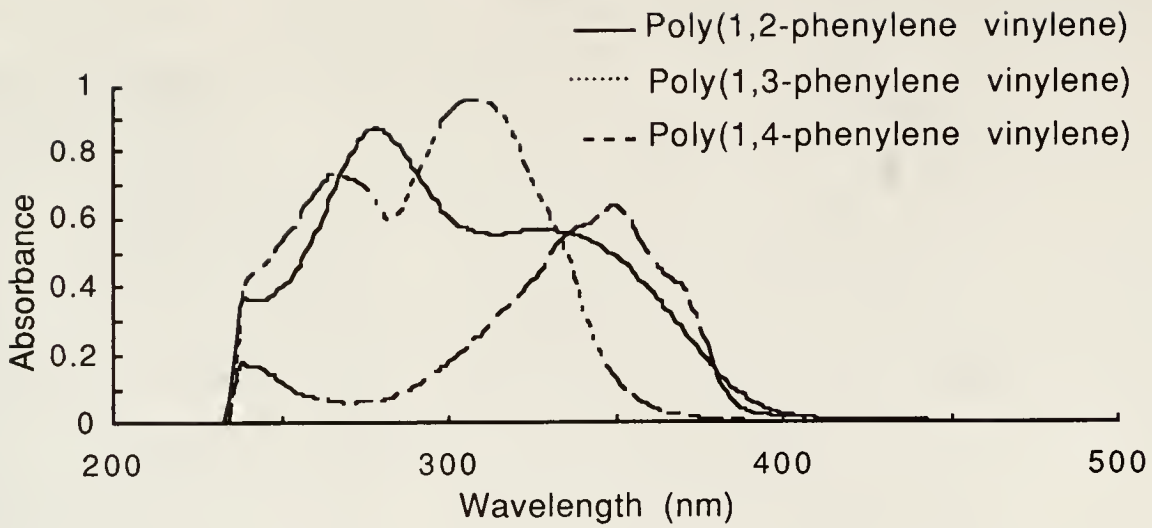


Figure 5.12. The UV spectra of three poly(phenylene vinylene).

Copolymerization of 1,2- and 1,3-Dipropenylbenzene with 1,9-Decadiene

Copolymerization of 1,2-dipropenylbenzene and 1,3-dipropenylbenzene with 1,9-decadiene was conducted under conditions different from previous work of copolymerization of 1,4-dipropenylbenzene with 1,9-decadiene.[161] Molybdenum catalyst 1c instead of tungsten catalyst 1a was used in the reaction, and polymerization was carried out at room temperature rather than at 50-60 °C. Molybdenum catalyst 1c was more effective for terminal dienes than for internal dienes; therefore, the rate of polymerization of 1,9-decadiene increases and the rate of polymerization of dipropenylbenzene decreases. These rate changes led to the changes in the copolymer structures.

Poly(1,2-phenylenevinylene-co-octenamer) (1:1) 46 was successfully obtained through ADMET copolymerization of equimolar 1,2-dipropenylbenzene and 1,9-decadiene at room temperature with intermittent application of a vacuum. In this copolymer chain, there were three possible double bond joints between phenylenes and hexamethylenes, phenylene-=-phenylene (PP), phenylene-=-hexamethylene (PH), and hexamethylene-=-hexamethylene (HH).

The ^{1}H NMR spectrum of copolymer 46 (Figure 5.13) display that the proton resonance for double bond of HH joint is at 5.38 ppm, proton resonances for double bond of PH joint was at 6.05 and 6.62 ppm, and proton resonance for double bond of PP joint is supposed to be at 7.1 ppm which was eclipsed by aromatic proton shifts. According to the integration of resonances, the ratio of PP:PH:HH for copolymer 46 was 10:73:17. It was surprising that only a very small amount of phenylene-=-phenylene segments were formed in the

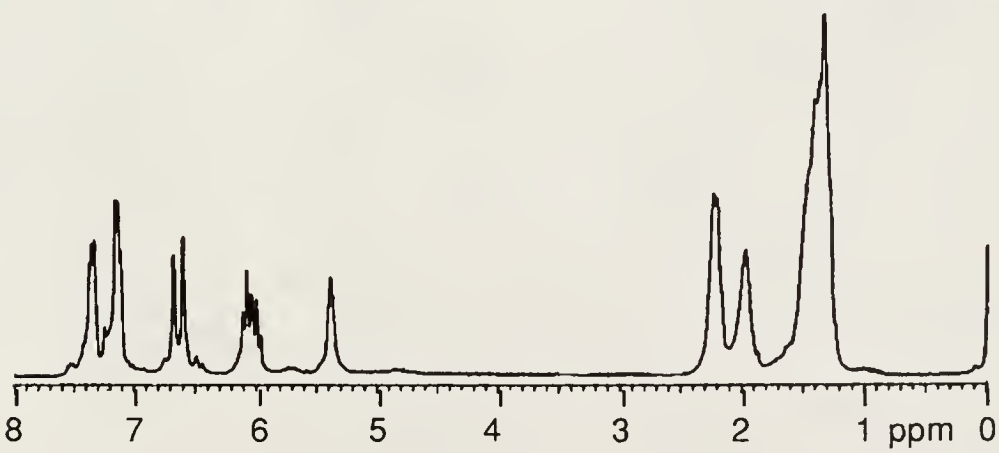


Figure 5.13. ^{1}H NMR spectrum of poly(1,2-phenylenevinylene-co-octenamer) (1:1) 46.

molecular chain. The major portion was phenylene-=-hexamethylene segments. The copolymer obtained here is a random copolymer, and this result is significantly different from the reported copolymerization of 1,4-dipropenylbenzene with 1,9-decadiene using tungsten catalyst at temperature of 50-60 °C, where a block copolymer was formed.[161]

The UV spectrum of copolymer 46 (Figure 5.14) was very close to that of the monomer 1,2-dipropenylbenzene, which showed that most phenylenes were individually separated by hexamethylenes. Comparison of the UV spectrum of copolymer 46 with those of monomer 1,2-dipropenylbenzene and poly(1,2-phenylene vinylene) confirmed that a random copolymer was formed.

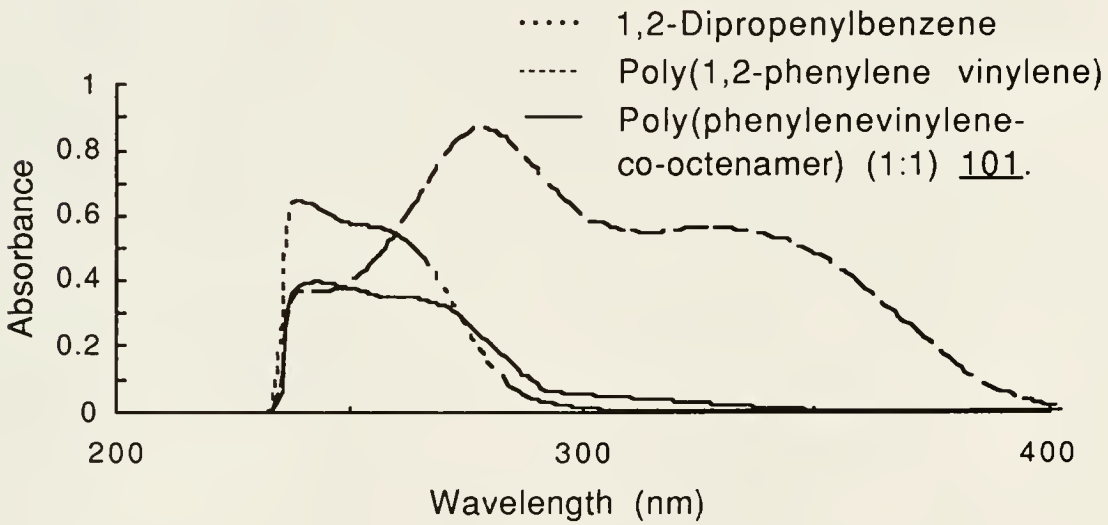


Figure 5.14. UV spectra of 1,2-dipropenylbenzene, poly(1,2-phenylene vinylene), and poly(1,2-phenylenevinylene-co-octenamer) (1:1).

Poly(1,2-phenylenevinylene-co-octenamer) (4:1) 47 and poly(1,2-phenylenevinylene-co-octenamer) (1:4) 48 were obtained

from monomer feed ratio (mole ratio of 1,2-dipropenylbenzene to 1,9-decadiene) of 4:1 and 1:4, respectively. In the copolymer 47 chain, nearly equal amounts of phenylene-=-phenylene (47.1%) and phenylene-=-hexamethylene (52.9%) segments were found in the polymer chain. The hexamethylene-=-hexamethylene segment was close to zero according to the analysis of the ^1H NMR spectrum. The UV absorption (Figure 5.15) of copolymer 47 was similar to that of poly(1,2-phenylene vinylene), which demonstrated that a certain amount of poly(1,2-phenylene vinylene) blocks were formed in copolymer 47.

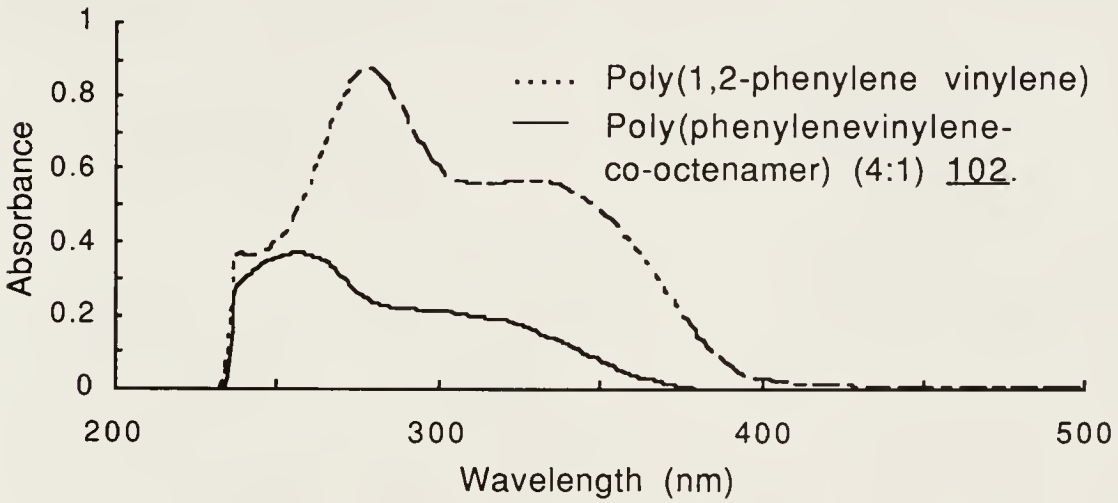


Figure 5.15. UV spectra of Poly(1,2-phenylene vinylene), and poly(1,2-phenylenevinylene-co-octenamer) (4:1).

When the monomer feed ratio of 1,2-dipropenylbenzene to 1,9-decadiene was 1:4, the obtained copolymer 48 showed no poly(1,2-phenylene vinylene) segments in the molecular chain. The ^1H NMR spectrum of the copolymer 48 (Figure 5.16) showed that the ratio of phenylene-=-hexamethylene to hexamethylene-=-hexametylene was

1:1.7. The UV absorbance of copolymer 48 (Figure 5.17) was the same as that of monomer 1,2-dipropenylbenzene, which

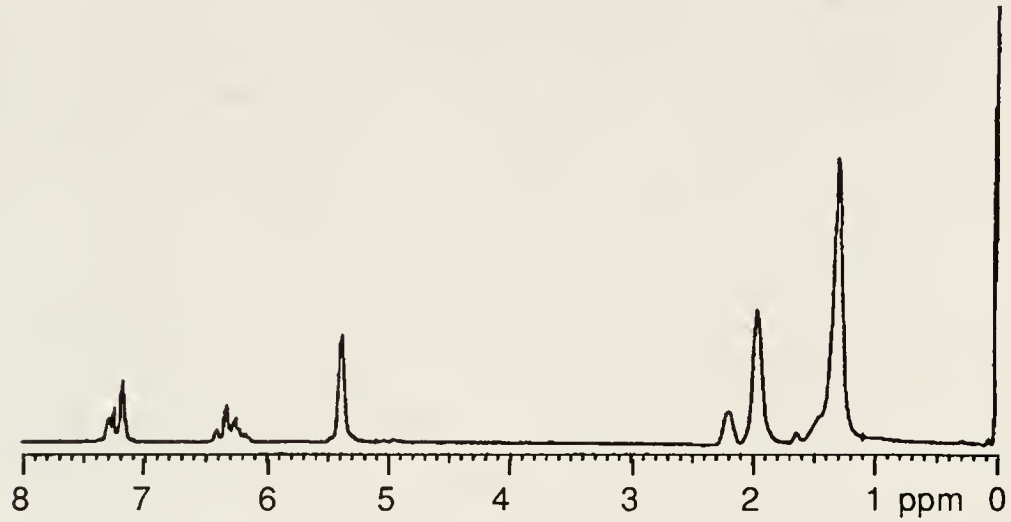


Figure 5.16. ^{1}H NMR spectrum of poly(1,2-phenylenevinylene-co-octenamer) (1:4) 103.

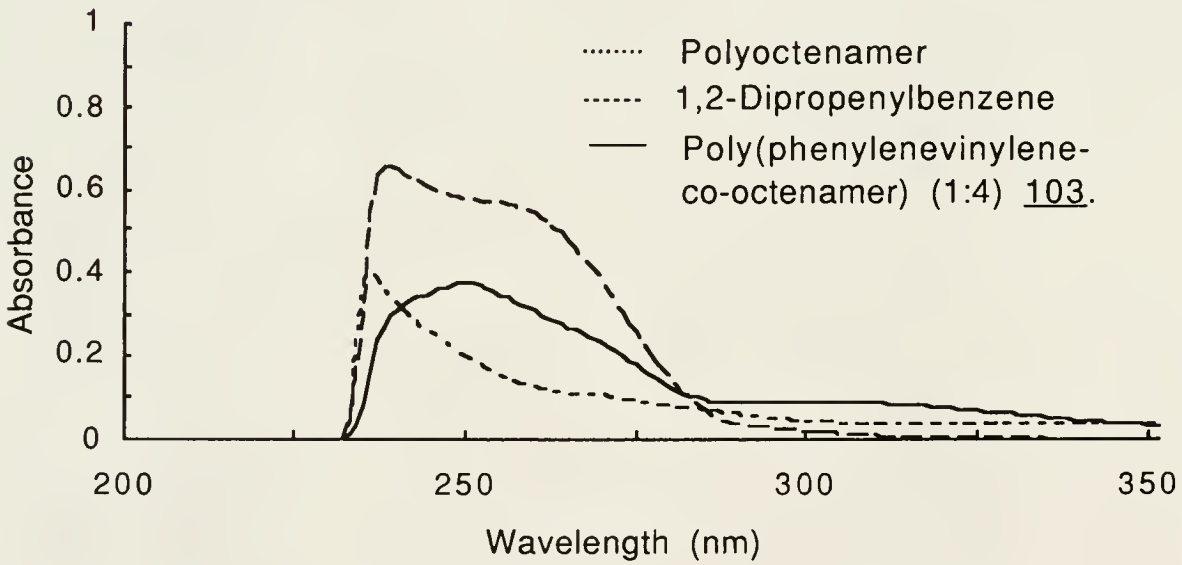


Figure 5.17. UV spectra of 1,2-dipropenylbenzene and poly(1,2-phenylenevinylene-co-octenamer) (1:4) 48.

demonstrated that there were no poly(1,2-phenylene vinylene) blocks in this copolymer, but that the polyoctenamer blocks were connected by phenylene vinylene units.

The molecular weight data of the copolymers 46, 47, and 48, determined by gel permeation chromatography, listed in Table 5.3, show that the molecular weight increased with increasing amounts of 1,9-decadiene in the monomer feed ratio.

Table 5.3. The molecular weight and its distribution of copolymers 46, 47, and 48 determined by GPC.

Mole Feed Ratio 1,2-DPB:1,9-Dec[a].	Mn	Mw	Mw/Mn
4:1	670	830	1.25
1:1	2100	3960	1.92
1:4	2110	4040	1.97

[a]1,2-DPB and 1,9-dec. refer to 1,2-dipropenylbenzene and 1,9-decadiene, respectively.

The ADMET polymerization is a progressive polymerization in which the catalyst is kept active, and thus the addition of a second monomer to a homopolymer chain is possible. Based on this idea, the synthesis of block copolymers was conducted via homopolymerization of one monomer first and then addition of a second monomer to produce copolymers.

The first such copolymerization contained the addition of 1,2-dipropenylbenzene into the polyoctenamer after the

homopolymerization of 1,9-decadiene was completed. When the same equivalent of 1,2-dipropenylbenzene was added to the solid polyoctenamer at room temperature, a uniform solution of polyoctenamer in 1,2-dipropenylbenzene was gradually formed with stirring. The polymerization continued for 36 h to completion. This copolymer 49 had a random structure that contained approximately 75% phenylene-=-hexamethylene segments, and about 12.5% of equal amounts of phenylene-=-phenylene and hexamethylene-=-hexamethylene segments, according to the analysis of the ^{1}H NMR spectrum (Figure 5.18). The UV absorbance for this copolymer was very similar to that of the monomer 1,2-dipropenylbenzene, which confirmed the random copolymer structure. The number average molecular weight (Mn) determined by GPC for this copolymer was 1400, and the weight average molecular weight (Mw) was 2300.

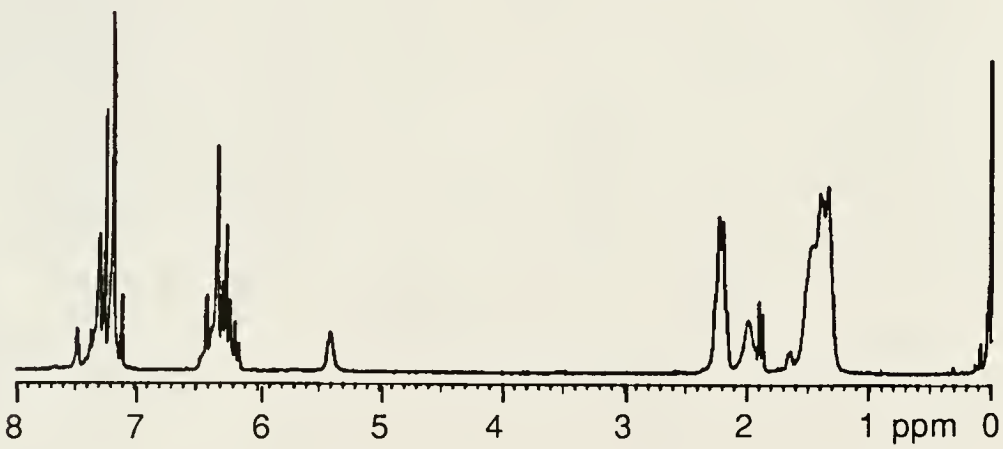


Figure 5.18. ^{1}H NMR spectrum of copolymer 104.

Copolymer 50, was obtained through addition of 1,9-decadiene to poly(phenylene vinylene). The ^{1}H NMR spectrum of polymer 50 (Figure 5.19) showed that this polymer was a copolymer, rather than

a mixture of two homopolymers, because the proton resonance of CH_2 group connected to the phenylenevinylene segment appeared at 2.2 ppm which was 0.2 ppm downfield of the CH_2 group in the regular octenamer segment, and the proton resonance of methyl end-group for poly(phenylenevinylene) disappeared. Poly(1,2-phenylenevinylene-co-octenamer) 50 looked more like a block copolymer according to the analysis of the ^1H NMR spectrum (Figure 5.19) and UV spectrum (Figure 5.20). Both phenylene-=-phenylene and hexamethylene-=-hexamethylene blocks were found in the ^1H NMR spectrum. The UV absorbance of copolymer 50, similar to that of poly(phenylene vinylene) showed that poly(1,2-phenylene vinylene) blocks existed in the copolymer 50. Formation of block copolymer 50 could be attributed to the poly(phenylene vinylene) insoluble in 1,9-decadiene, therefore the second monomer would prefer to add to the chain end instead of being inserted to the polymer chain as was observed in copolymer 49.

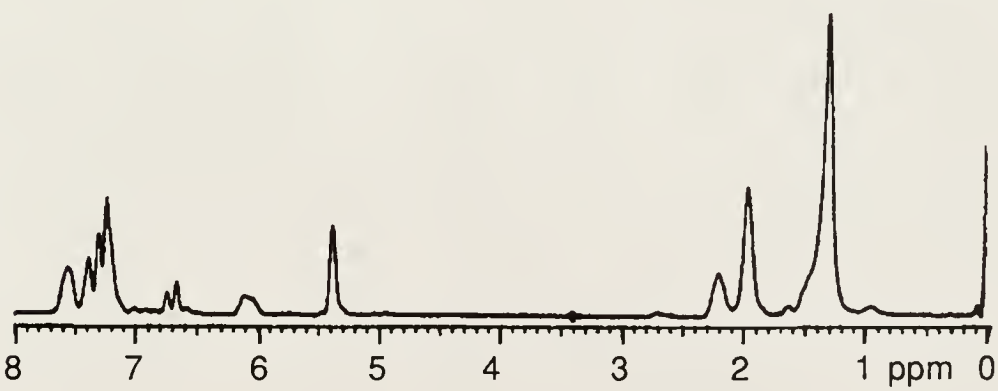


Figure 5.19. ^1H NMR spectrum of copolymer 50.

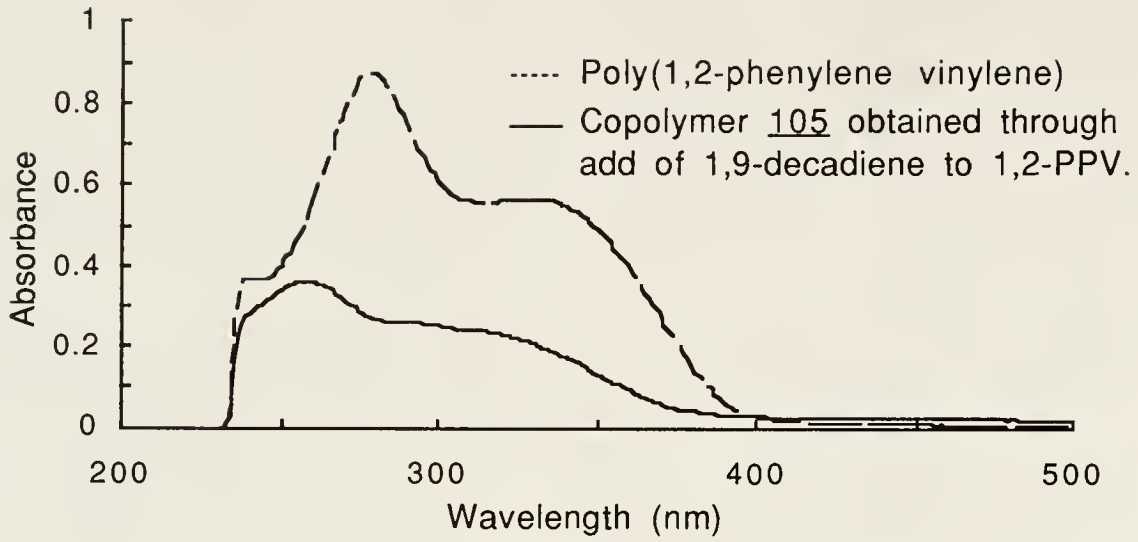


Figure 5.20. UV spectrum of copolymer 50 and poly(1,2-phenylene vinylene).

Poly(1,3-phenylenevinylene-co-octenamers) 51, 52, and 53 were obtained through ADMET copolymerization of 1,3-dipropenylbenzene and 1,9-decadiene using monomer feed ratios (mole ratio of 1,3-dipropenylbenzene to 1,9-decadiene) 4:1, 1:1, and 1:4, respectively. These three copolymers had basically the similar structures to those of poly(1,2-phenylenevinylene-co-octenamers). Table 5.4 lists the molecular weight of three copolymers determined by GPC. The number average molecular weight for copolymer 52 was 610, for copolymer 51 was 1240, and for copolymer 53 was 2640, which increased with increasing amounts of 1,9-decadiene in the initial monomer feed.

Table 5.4. The molecular weight and its distribution of copolymers 51, 52, and 53 determined by GPC.

Mole Feed Ratio 1,3-DPB:1,9-Dec[a].	Mn	Mw	Mw/Mn
4:1	610	790	1.30
1:1	1240	1720	1.28
1:4	2640	5790	2.20

[a]1,3-DPB and 1,9-dec. refer to 1,3-dipropenylbenzene and 1,9-decadiene, respectively.

Discussion of Reactivities Between Conjugated Dienes and Nonconjugated Dienes

The ADMET copolymerization of 1,4-dipropenylbenzene and 1,9-decadiene had produced block copolymers according to the previous research.[161] Also a much faster polymerization rate for 1,4-dipropenylbenzene than that for 1,9-decadiene has been observed, which suggested that the double bond conjugated with the benzene ring had a higher reactivity than did the double bond connected with the alkyl backbone. In order to investigate the competitive reactivities of 1,4-dipropenylbenzene and 1,9-decadiene, a model monomer, 8-octenyl-*p*-propenylbenzene (see Figure 5.21), was synthesized and polymerized. In this monomer, one double bond was connected with a hexamethylene group, and another double bond was connected with a phenylene group.

If it were true that the reactivity of the ene group connected with phenylene was much higher than the ene group connected with hexamethylene, then the polymerization of 8-octenyl-*p*-propenylbenzene would go through route 1 in Figure 5.21 to produce a polymer which had alternate phenylene-=-phenylene and hexamethylene-=-hexamethylene segments. Otherwise a random polymer would be produced (Figure 5.21, route 2).

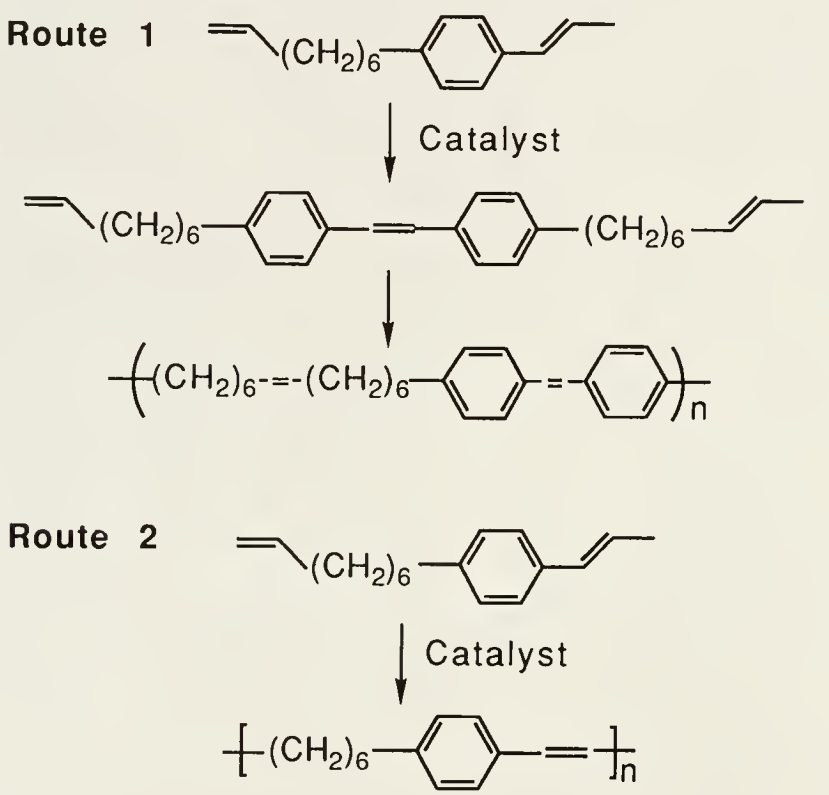


Figure 5.21. Polymerization of 8-octenyl-p-propenylbenezene.

The actual polymer obtained from ADMET polymerization of 8-octenyl-p-propenylbenezene was soluble in toluene and had a average degree of polymerization of 10. The polymer contained one phenylene-=-phenylene segment, two hexamethylene-=-

hexamethylene segments, and six phenylene-=-hexamethylene segments according to ^1H NMR spectra (Figure 5.22). This result conflicts with previous work[161] on the formation of a block copolymer, and the reactivity of different ene groups remains unclear.

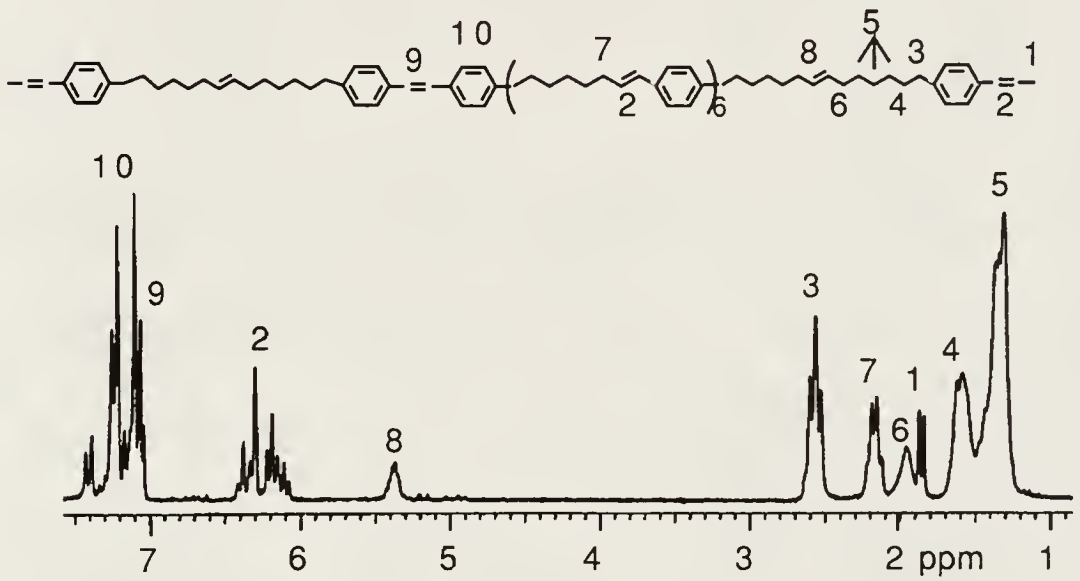


Figure 5.22. ^1H NMR spectrum of poly(hexamethylene phenylene vinylene).

The copolymers obtained in copolymerization of 1,2- and 1,3-dipropenylbenzene with 1,9-decadiene had a random statistical structure as described in the previous section. Table 5.5 lists the distribution of three segments in the copolymers with different initial feed ratios. When 1,2-dipropenylbenzene was 20% in the monomer feed ratio, no phenylene-=-phenylene segments were found. When 1,2-dipropenylbenzene was 80% in the monomer feed ratio, 47% of phenylene-=-phenylene segments were found. The phenylene-=-hexamethylene segments were the predominant with a 50:50

monomer feed ratio in both poly(1,2-phenylenevinylene-co-octenamer) and poly(1,3-phenylenevinylene-co-octenamer) copolymers. It was surprising to find that the polymerization of 8-octenyl-p-propenylbenezene using tungsten catalyst produced a polymer which had a very similar structure (see Table 5.5) to that of poly(1,2-phenylenevinylene-co-octenamer) (50:50) and poly(1,3-phenylenevinylene-co-octenamer) (50:50) copolymers.

Table 5.5. The segment ratios of phenylene-=-phenylene, phenylene-=-hexamethylene, and hexamethylene-=-hexamethylene in poly(1,2-phenylenevinylene-co-octenamer), poly(1,3-phenylenevinylene-co-octenamer), and poly(hexamethylene phenylenevinylene).

Monomer Feed Ratio	phenylene-=-phenylene %	phenylene-=-hexamethylene %	hexamethylene-=-hexamethylene %
1,2-DPB:1,9-decadiene[a]	Poly(1,2-phenylenevinylene-co-octenamer)		
80:20	47	53	0
50:50	10	73	17
20:80	0	37	63
1,3-DPB:1,9-decadiene[a]	Poly(1,3-phenylenevinylene-co-octenamer)		
80:20	61	39	0
50:50	15	67	18
20:80	0	39	61
8-octenyl-p-propenylbenzene	Poly(hexamethylene phenylenevinylene)		
	11	67	22

[a]1,2-DPB and 1,3-DPB refer to 1,2- and 1,3-dipropenylbenzene.

For further investigation of the reactivity ratio of conjugated dienes and nonconjugated dienes in copolymerization, a model study of a metathesis reaction between propenylbenzene and 1-nonene was conducted using the molybdenum catalyst at room temperature (Figure 5.23). This model study was based on the fact that the reactivity of a functional group is independent of the size of the molecule to which it is attached.[166] These simplifying assumptions make the kinetics of step polymerization identical to those for the analogous small molecule reaction. Therefore, the suggested monoolefin metathesis reaction should be analogous to the ADMET copolymerization of diene monomers.

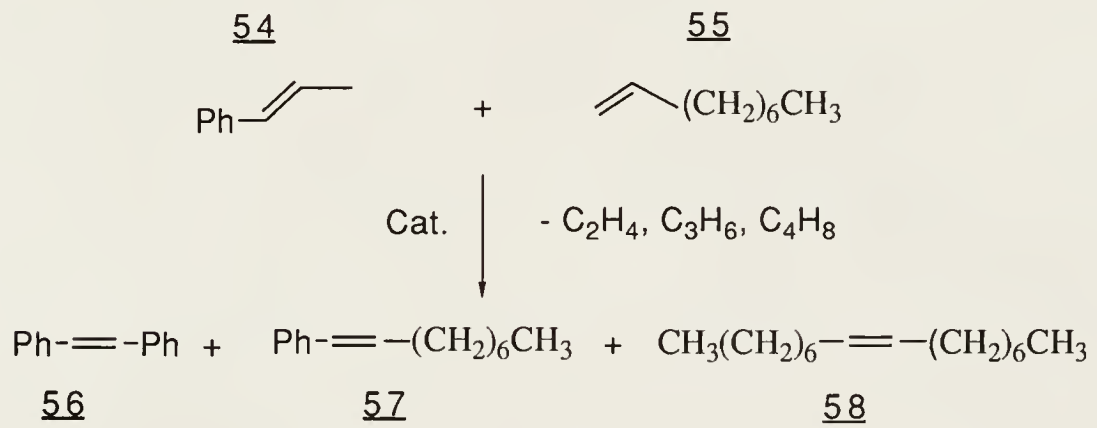


Figure 5.23. Metathesis reaction of propenylbenzene and 1-nonene.

The products obtained from this metathesis reaction were compounds 56, 57 and 58 (Figure 5.23). The percent ratios of the three products were determined by the integration of ^1H NMR spectra, which were summarized in Table 5.6. A random distribution of the products was obtained.

Table 5.6. The percent of products 56, 57 and 58 in metathesis reaction of propenylbenzene and 1-nonene.

Percent of Ph-=-CH_3 in initial mixture	Product 56 %	Product 57 %	Product 58 %
0	0	0	100
10	0	20	80
30	5	50	45
50	17	66	17
70	60	20	20
90	85	10	5
100	100	0	0

Figure 5.24 showed theoretical statistical distribution values and experimental values for the products 56, 57, and 58 in monoolefin model reaction. A consistency between statistical values and experimental values was observed in Figure 5.24. The three lines were the theoretically statistical values for percents of compounds 56, 57, 58, which were calculated according to the method described in the literature.[85] The dots represented experimental values for the three products. Comparison of ratios of the phenylene-=-phenylene, phenylene-=-hexamethylene, and hexamethylene-=-hexamethylene in the monoolefin model reaction (see Table 5.6) with those in poly(1,2-phenylenevinylene-co-octenamer), poly(1,3-phenylenevinylene-co-octenamer) copolymers, and poly(hexamethylene phenylenevinylene) (see Table 5.5), demonstrated that a random distribution occurred in both the small

molecule reaction and copolymerization. We can conclude that, using the molybdenum catalyst 1c at room temperature, the copolymerization of dipropenylbenzene and 1,9-decadiene produced copolymer having a random structural distribution that depended statistically upon the initial monomer feed ratio.

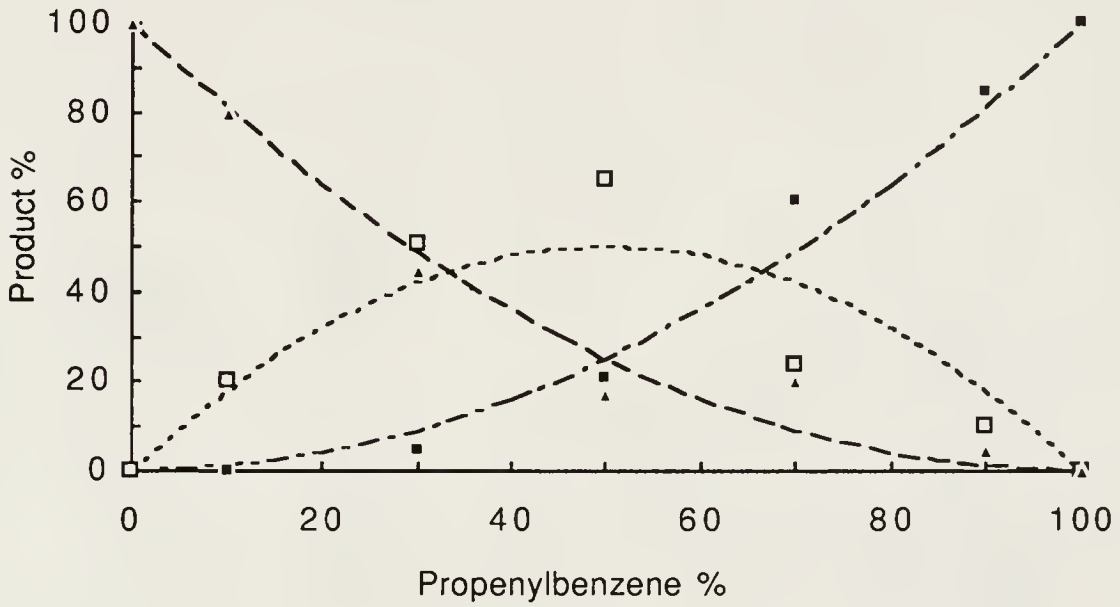


Figure 5.24. The statistical values and experimental values for the products from metathesis reaction of propenylbenzene and 1-nonene.
▲, □, and • represent experimental values for compounds 56, 57, and 58.
- - -, ·····, and —— represent statistical values for compounds 56, 57, and 58.

Conclusions

Poly(1,2-phenylene vinylene) oligomer and poly(1,3-phenylene vinylene) oligomer were synthesized through ADMET polymerization of 1,2-dipropenylbenzene and 1,3-dipropenylbenzene, respectively. Copolymerization of 1,2-dipropenylbenzene and 1,3-dipropenylbenzene with 1,9-decadiene produced copolymers having random statistical structures, which were based on the initial monomer feed ratios. The structural distributions of poly(1,2-phenylenevinylene-co-octenamers) and poly(1,3-phenylenevinylene-co-octenamers) were different from the previous work of poly(1,4-phenylenevinylene-co-octenamer), where block copolymers were obtained. The addition of 1,9-decadiene to poly(1,2-phenylene vinylene) produced a block copolymer, and the addition of 1,2-dipropenylbenzene to polyoctenamer, however, produced a random copolymer.

CHAPTER 6

SUMMARY OF DISSERTATION

Acyclic diene metathesis (ADMET) polymerization is a step, condensation reaction which has proven to be a viable synthetic route to high molecular weight unsaturated polymers and copolymers. Since the first successful ADMET polymerization achieved in 1988, a number of unsaturated polymers containing ether, ketone, ester, carbonate, silane, and thioether functionalities, have been synthesized. Lewis acid free catalysts such as Schrock's tungsten and molybdenum compounds are required. Prior to this dissertation, only those monomers, where a spacer group was present between the two terminal olefins, had been used in ADMET polymerization.

This dissertation describes a study of the chemistry of conjugated monomers in ADMET polymerization. Conjugated monomers include those in which two olefins are connected together, such as 2,4-hexadiene and 1,3-butadiene. Furthermore, monomers where the two olefins are connected by a phenylene group, such as 1,2-dipropenylbenzene and 1,3-dipropenylbenzene are also been investigated. ADMET homopolymerizations and copolymerizations of the conjugated monomers have been conducted, and the reactivities of those monomers in ADMET polymerization have been examined.

The internal diene, 2,4-hexadiene, was the first to be examined in ADMET polymerization, and methyl terminated polyacetylene oligomers were successfully obtained via bulk polymerization. The NMR spectra of these polyacetylene oligomers clearly showed that methyl groups were present at both ends of the polyacetylene chain. According to the ^{1}H NMR integration values, these polyacetylene oligomers possessed an average of 6-10 repeat units (double bond). Mass spectrometry (MS) showed that the highest detectable length is 20 repeat units, and gel permeation chromatography (GPC) vs. polybutadiene standards showed an average of 15 repeat units. Only polyacetylene oligomers were produced because the methyl terminated polyacetylenes have high melting points (4-ene, mp 115 °C; 5-ene, mp 150 °C) and solidify at low degrees of polymerization. In this manner, the terminal olefins of the polyacetylene oligomers are restricted from further metathesis condensation. The multiple UV absorptions of these polyacetylene oligomers were attributed to the different polyacetylene chain lengths.

Solution polymerization of 2,4-hexadiene (in benzene) produced polyacetylenes with an average of 10-15 double bond units as determined by NMR spectroscopy. Mass spectrometry (MS) showed that the highest detectable length is 21 repeat units, and gel permeation chromatography (GPC, polybutadiene standards) showed an average of 20 repeat units. The UV spectrum of the solution polymerization product exhibited higher wavelength absorptions than did the bulk polymerization product.

Polyacetylene oligomers obtained through the bulk polymerization of 2,4,6-octatriene had molecular lengths and physical properties similar to those obtained from the bulk polymerization of 2,4-hexadiene.

The terminal diene, 1,3-butadiene, and the terminal triene, 1,3,5-hexatriene were not active in ADMET polymerization. Bulk polymerization of 1,3-butadiene did not produce any observable ADMET polymer, and only unreacted monomer remained in the reaction system. The molybdenum catalyst apparently decomposed, although it is not clear how 1,3-butadiene played a role.

The conjugated terminal triene, 1,3,5-hexatriene, exhibited the same non-ADMET reactivity with the molybdenum catalyst as did 1,3-butadiene. The molybdenum catalyst decomposed faster in 1,3,5-hexatriene than in 1,3-butadiene.

Copolymerizability of 2,4-hexadiene with nonconjugated dienes has also been studied. The copolymerization of 2,4-hexadiene and a nonconjugated terminal diene, 1,9-decadiene, was not successful using either tungsten or molybdenum catalysts. 1,3-Butadiene was formed through a metathesis exchange reaction between 2,4-hexadiene and 1,9-decadiene, and subsequently the catalyst was decomposed by the newly formed 1,3-butadiene.

Poly(acetylene-co-octenamer) copolymers have been successfully synthesized through copolymerization of 2,4-hexadiene and 2,10-dodecadiene using monomer mole ratios (2,4-hexadiene to 1,9-decadiene), 4:1, 2:1, 1:1, 1:2, and 1:4, respectively. Block copolymers were obtained according to the analysis of ^{1}H NMR spectra and UV spectra.

Attempted polymerization of functional group-terminated 1,3-butadienes to produce telechelic polyacetylene has been investigated. ADMET polymerization of *trans,trans*-1,4-diphenyl-1,3-butadiene was not successful. The ^1H NMR spectrum showed that the molybdenum catalyst and the monomer remained unreacted during the course of the experiment. This inactivity could be attributed to the steric hindrance of the phenyl units. The linear conjugated *trans,trans*-1,4-diphenyl-1,3-butadiene is too large to access the metal center to form the metallacyclobutane. Therefore, the reaction between the monomer and the catalyst was prevented.

The monomer *cis,cis*-1,4-dicyano-1,3-butadiene was not productive in ADMET polymerization as well. A reaction between *cis,cis*-1,4-dicyano-1,3-butadiene and molybdenum catalyst, however, was observed. A new alkylidene resonance appeared at 13.93 ppm in the ^1H NMR spectrum. The proton resonances in the alkoxy group $OCCH_3(CF_3)_2$ and in the aromatic imido group N-2,6-C_6H_3-$[CH(CH_3)_2]_2$ of the catalyst were moved downfield as well. These shifts of the ^1H NMR resonances of the molybdenum complex may be caused by the formation of a coordination between *cis,cis*-1,4-dicyano-1,3-butadiene and the molybdenum catalyst, or by the occurrence of metathesis exchange reaction between this monomer and the catalyst forming a new alkylidene complex.

A method for the synthesis of telechelic polymers via ADMET polymerization of dienes and monoolefins has been examined. Isobutyl-terminated polyoctenamer has been successfully synthesized through ADMET polymerization of 1,9-decadiene with 4-methyl-1-pentene. Polymerization of 2,4-hexadiene with 4-

methyl-1-pentene, however, did not produce isobutyl-terminated polyacetylene. In this reaction, 1,3-butadiene was formed by a metathesis exchange reaction between 2,4-hexadiene and 4-methyl-1-pentene, and subsequently decomposed the molybdenum catalyst.

The successful synthesis of telechelic polyacetylenes was achieved through the ADMET polymerization of 2,4-hexadiene with internal monoolefins. Hexyl-, phenyl-, trimethylsilyl-, and 3-yl acetate-1-propyl-terminated polyacetylene have been synthesized by reaction of 2,4-hexadiene with 7-tetradecene, propenylbenzene, 1,4-trimethylsilyl-2-butene, and 4-octen-1,8-diyl acetate, respectively.

ADMET reactivities of conjugated monomers, 1,2- and 1,3-dipropenylbenzene have been studied. Poly(1,2-phenylene vinylene) and poly(1,3-phenylene vinylene) oligomers were synthesized through ADMET polymerization of 1,2-dipropenylbenzene and 1,3-dipropenylbenzene, respectively. According to the integration of the ^{1}H NMR spectra, the average degree of polymerization for poly(1,3-phenylene vinylene) was 4, and poly(1,2-phenylene vinylene) was 8. The reason for only producing oligomers was that the conjugated oligomers had a regular configuration and were easily coagulated and precipitated from the reaction system. In this manner, the terminal olefins of the oligomers were restricted from further metathesis condensation.

ADMET copolymerization of 1,2-dipropenylbenzene and 1,3-dipropenylbenzene with 1,9-decadiene have been conducted in various methods using the molybdenum catalyst. Poly(1,2-phenylenevinylene-co-octenamers) have been successfully obtained

through ADMET copolymerization of 1,2-dipropenylbenzene and 1,9-decadiene using monomer feed ratios (mole ratio of 1,2-dipropenylbenzene to 1,9-decadiene), 4:1, 1:1, and 1:4, respectively. According to the analysis of NMR, UV, and a model reaction of propenylbenzene and 1-nonene, the copolymers have random statistical structures which are based on the initial monomer feed ratios. The addition of 1,9-decadiene to poly(1,2-phenylene vinylene) produced a block copolymer, and the addition of 1,2-dipropenylbenzene to polyoctenamer, however, produced a random copolymer. The weight average molecular weight of poly(1,2-phenylenevinylene-co-octenamers) increased from 800 to 4000 with increasing amounts of 1,9-decadiene in the monomer feed from 30% to 80%.

Poly(1,3-phenylenevinylene-co-octenamers) were obtained through ADMET copolymerization of 1,3-dipropenylbenzene and 1,9-decadiene using monomer feed ratios (mole ratio of 1,3-dipropenylbenzene to 1,9-decadiene) 4:1, 1:1, and 1:4, respectively. These three copolymers have basically the same random structures to those of poly(1,2-phenylenevinylene-co-octenamers).

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BIOGRAPHICAL SKETCH

The author was born in Nantong, Jiangsu Province, the People's Republic of China, on April 25, 1946, a year after World War II ended and the Third Civil War of China began. After completion of his primary school and secondary school education, he entered Tsinghua University in 1964. His education was interrupted by the so-called "cultural revolution" during the end of his second year of undergraduate study. Upon graduating in 1971, he was assigned to teach in a high school for 7 years. He went back to graduate school at Tsinghua University to study polymer science in 1979, when graduate schools in China were reopened again. After he received his master's degree, he went to do adhesives research at a research institute for 6 years. In 1989, he came to Gainesville, Florida, to begin graduate studies in organic/polymer chemistry at the University of Florida under the direction of Dr. K. B. Wagener and completed his graduate studies in April, 1994.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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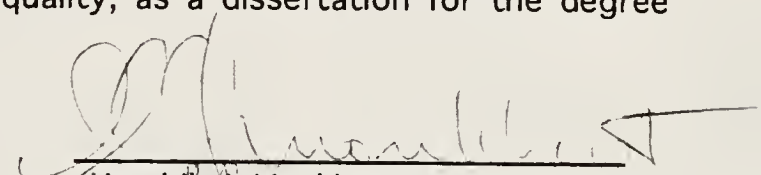

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